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MANUAL ON POLLUTION-PREVENTION AND SAFETY

In Connection With
The Deep Sea Drilling Project (DSDP)

and

The International Phase of Ocean Drilling (IPOD)

By

JOIDES PANEL ON
POLLUTION-PREVENTION AND SAFETY

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I. INTRODUCTION

The only way to be absolutely certain of safety and of freedom from hazards of pollution in connection with drilling in the oceans is to do no drilling at all. Any drilling involves some risk. The value of the scientific objectives that are sought must be balanced against potential hazards so that the program will achieve these objectives so far as possible without falling below acceptable standards either of safety or for the prevention of pollution.

It is the unanimous opinion of the Panel, considering the possible value of the results to be obtained and after weighing the safety measures which can reasonably be taken, that risks can be so minimized through planning and operational procedures that the major objectives of the program can always be obtained. The Panel emphasizes, however, that adherence to the old adage of "An ounce of prevention is worth a pound of cure" offers the highest benefit-cost ratio for safety and pollution-prevention. A few dollars spent on extra care in preliminary site surveys and in planning of the drilling program may forestall an accident which could not only cause lamentable loss of life and property and damage to the environment but could also cause the abrupt termination of the whole DSDP.

This November 25, 1975, revised edition of the Manual has been prepared with recognition of the approaching Phase 4, International Phase of Ocean Drilling (IPOD), of the Deep Sea Drilling Project (DSDP), scheduled to start this fall with Leg 45. The diverse sites of IPOD will involve some additional hazards over those of previous DSDP drilling, in that deeper sediment penetrations (with re-entries) are scheduled for many margin sites and, on the margins, more holes may be drilled in relatively shallow water than heretofore. Moreover, it now seems probable that at least for the first years of IPOD there will be little change in the drilling equipment available on the GLOMAR CHALLENGER and that IPOD must continue to face the safety hazards of DSDP inherent in lack of riser pipe to the surface, lack of return circulation, and lack of blowout preventers. However, it is still the hope of this Panel that a well logging capability may be established on board before very thick sediment drilling is undertaken, and it is also hoped that more adequate seismic information will be available on IPOD holes than on many of the previous holes. In any case it seems evident that safety and pollution-prevention aspects of the program should continue to receive as great or greater emphasis than before. It is recommended that this Manual be given wide distribution to all concerned with DSDP-IPOD program and operations.

II. PRINCIPAL HAZARDS

A. Oil and Gas Escape and Blowouts

The principal hazard in ocean drilling, with respect to safety and pollution-prevention, comes from the possibility of opening up

reservoir strata which would allow oil or hydrocarbon gas to escape in large quantities into the sea or the atmosphere.

Natural submarine seepages both of oil and of gas exist in many parts of the world, apparently with little deleterious effect on the environment, and it is difficult to say what amounts of oil or gas released into the sea water or the atmosphere by drilling operations should be termed hazardous as regards environmental considerations. Certainly as a pollutant, escaping oil must be considered far more serious than escaping gas.

On the other hand, as a hazard to safety of personnel and property, hydrocarbon gas may be even more dangerous than oil because of its mobility, highly flammable nature, and the difficulties in its pressure control.

Offshore drilling for oil is currently taking place along much of the world's marine coastline and, on the whole, exhibits a remarkable safety record. However, it must be recognized that, in any drilling operation, release of hydrocarbons can occur if adequate precautions are not taken and that this can be hazardous both as regards pollution and safety. Since DSDP drilling is particularly vulnerable in this respect because of the limited controls available from the GLOMAR CHALLENGER, it has seemed particularly important both for pollution and safety considerations to try to avoid entirely any substantial release of either oil or gas during its operations, either into the sea or the atmosphere, whether through quiet escape or through violent blowouts. Moreover, regardless of pollution or safety effects, the waste of gas or oil by careless dissipation into the oceans might bring about a serious menace to the DSDP from owners or potential owners of this resource in these days of emphasis on energy conservation.

1. Hydrocarbon origin and occurrences

The term petroleum may be applied to any dominantly hydrocarbon substance -- liquid, gas, or solid -- originating in the rocks of the Earth, although it is popularly reserved for the crude oil, natural gas, and asphalt of the so-called petroleum industry.

Mixtures of petroleum hydrocarbons exist as gaseous, liquid, and solid phases depending on the temperature, pressure, and composition of the system. Under natural surface conditions, C_1 - C_4 hydrocarbons -- such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}) -- are predominantly in the gas phase while C_5 and higher hydrocarbons -- such as pentane (C_5H_{12}), hexane (C_6H_{14}), etc. -- are predominantly liquid.

Hydrocarbon gases -- largely methane -- may be generated in significant quantities from organic matter in sediments either under near-surface conditions by bacterial action, or at generally greater depths by thermochemical action. Liquid petroleum (oil), however, is almost exclusively the product of thermochemical generation from hydrogen-rich organic matter in deeply buried sediments. This generation

appears to become quantitatively important only as temperatures in excess of 40-50°C are reached -- burial depths of 1000-1500 m for average geothermal gradients. Hydrocarbon gases are generated with the oil and, although consisting largely of methane, usually include significant quantities of ethane, propane, butane, etc. Thermochemical conversion of organic matter to hydrocarbons will continue to depths and temperatures at which all organic matter and the oil itself has been converted to methane and carbon residue.

The supposed relation of gas and liquid hydrocarbons of different modes of genesis to depth and temperature is shown diagrammatically in Figure 1. It should be stressed, however, that while biogenic hydrocarbons are generated at relatively shallow depths and thermochemical hydrocarbons at relatively greater depths, either may be found at any drilling depth in the sedimentary section, due to the results of migration or either subsequent burial or exhumation.

Biogenic methane is commonly found in swamps where it is known as "marsh gas," but it is also formed in marine sediments. Biogenic methane can be distinguished from thermochemical methane by means of the mass spectrograph -- the biogenic form has a distinctly higher ratio of the light carbon isotope C^{12} to the heavy carbon isotope C^{13} . Also, thermochemical methane generally shows a lower methane/ethane ratio than does biogenic methane, although some thermochemical methane is lacking in ethane and it now seems evident also that under some circumstances some ethane may be generated biochemically along with methane.

A discussion of the maturation characteristics of organic matter in sediments by George Claypool of this Panel is given in Appendix C-1.

Both biogenic and thermochemical methane may be expected to be encountered under respectively appropriate conditions in DSDP holes. There is little or no difference in their common physical and chemical properties. Both can cause blowouts, both can catch fire, both can be associated with some ethane, and both can occur in substantial quantities at very shallow depths. About the only major difference in significance is that the conditions which produce thermochemical methane may also produce liquid oil, whereas biogenic oil is unknown.

There is a common fallacy that if methane can be identified as biogenic, it can be disregarded as a threat to safety, but this is not so. (At least one serious blowout has occurred in offshore drilling operations due to gas of apparent biogenic origin - Cook Inlet, Alaska - and some commercial accumulations of purely biogenic methane are known.) Also it has been mistakenly suggested that if methane/ethane ratios are greater than a certain value, gas dangers can be dismissed because it is then a question of only "marsh gas," not "true petroleum gas"! Similarly, it has been said that shallow gas cannot be dangerous because it is "probably only biogenic"! Further, it has been irresponsibly suggested that on board the GLOMAR CHALLENGER certain levels of ethane content or concentration or of C^{12} - C^{13} ratios be set as critical limits beyond which no danger need be anticipated.

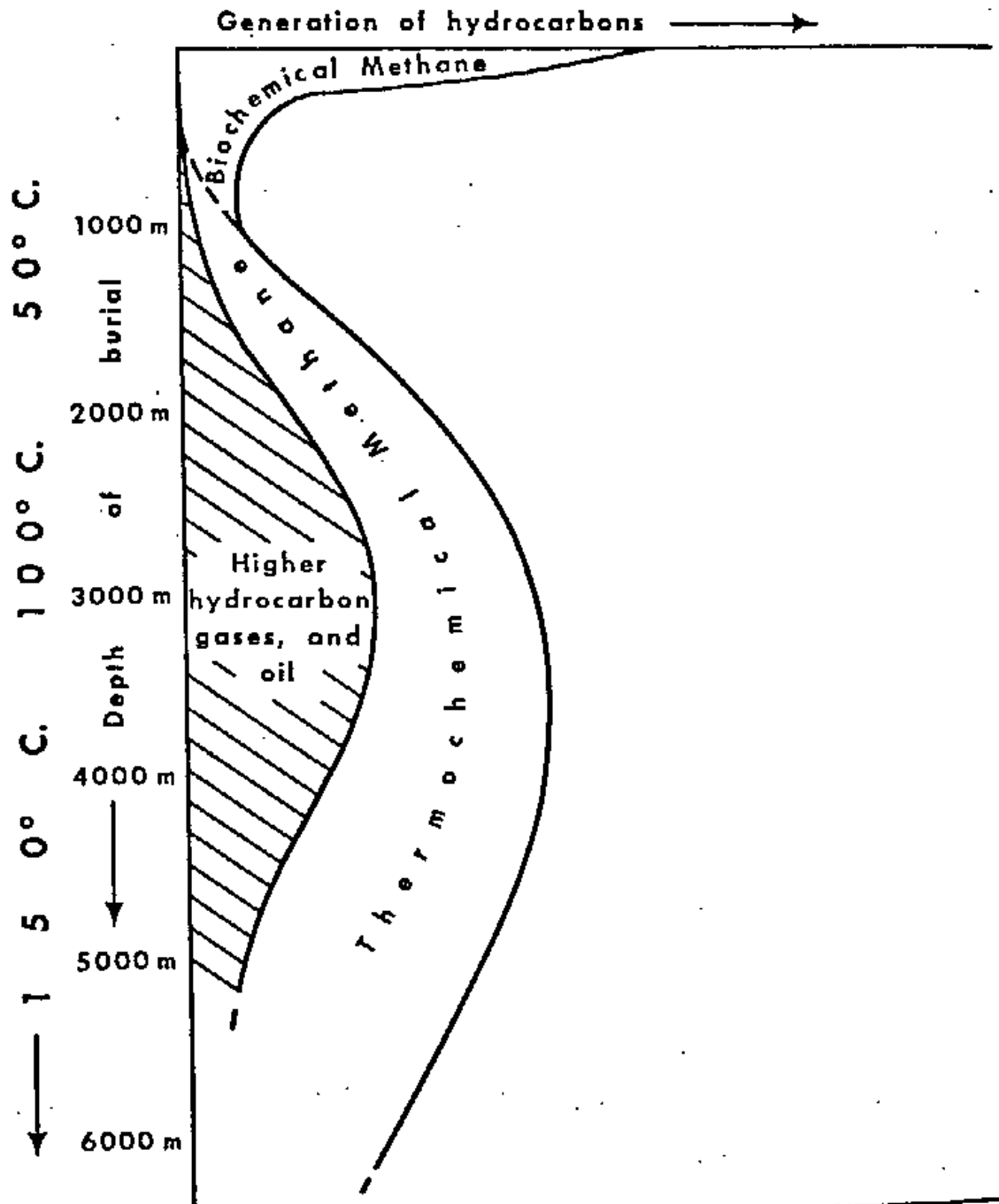


Figure 1. Suggested relation of generation of methane and higher hydrocarbons to depth of burial and temperature, and relation between genesis of biochemical (biogenic) methane and thermochemical methane. (Amplification and modification by Hedberg, 1974, of a sketch by V. A. Sokolov, reproduced by Kartsev et al., 1971.)

The Panel is, and has been, strongly in favor of getting as much information as possible on the character of the hydrocarbons encountered in the DSDP holes, but it would deplore, as a menace rather than an aid to safety, the setting of "magic numbers" of this sort as substitutes for balanced judgment based on the multitude of geological, geochemical, operational, and experience factors which should enter into the decision in any specific case. It believes that such arbitrarily imposed numerical limits are dangerous since the values must vary so much with other factors and circumstances, and since they are so likely to be used blindly as crutches to avoid sounder and more reasoned judgment. As we have stated many times, no one seems to have been able to convince the molecules of marsh gas or biogenic methane or "protopetroleum" that they have no right to accumulate, or blow out, or burn, or contaminate, just because they are not "true petroleum" or are not associated with other products of thermal maturation!

2. Cause and explanation of blowouts

In oil well drilling operations, formation fluid (water, oil, or gas, as the case may be) will flow from reservoir strata into the well bore whenever a substantial pressure-differential exists between the formation fluid and the drilling mud in the hole, that is, whenever the pressure of the fluid in the interstices of a reservoir formation substantially exceeds the adjacent pressure in the drill hole resulting from the weight of the column of drilling fluid filling the hole. The formation fluid entering the well bore is generally less dense than the drilling fluid and therefore will tend to move upward in response to gravity, once it has entered the hole.

When the formation fluid is gas, gas-charged oil, or gas-charged water, the gas, on entering the hole, may permeate the drilling fluid causing it to become "gas-cut" (filled with gas bubbles) and thus greatly diminishing its density and its ability to cause back-pressure on the formation. Likewise, when gas enters the well bore, it undergoes rapid expansion due to pressure reduction while travelling up the hole. Because the drilling fluid is confined by the narrow diameter of the bore hole (commonly less than 10 inches), the increasing expansion of the gas bubbles in the drilling fluid as they move upward will cause a flow of displaced drilling mud from the mouth of the hole, with further consequent reduction of the total weight of the fluid column in the hole, resulting in further reduction of the restraining pressure on the entry of formation fluid. The consequence is a sort of chain reaction. Gas will tend to enter the hole at an ever-accelerating rate as the pressure differential between formation and hole is increased, and, if not promptly brought under control, this may quickly result in violent ejection of all drilling fluid from the hole which in turn will result in "wild" or unrestrained flow of gas or gas-charged formation fluid at the surface. Such a calamitous event is called a "blowout" and may be extremely dangerous to life, property, and environment. Elaborate measures are employed by the industry to prevent

its occurrence -- weighting of drilling muds, application of back pressure by pumps, use of mechanical blowout preventers, etc.

3. Differences in blowout risks between DSDP and oil well drilling operations

In current Deep Sea Drilling Project (DSDP) operations, conditions are in some respects quite different from those of customary oil well drilling, principally due to lack of means for return circulation, the use of sea water as drilling fluid, the lack of any confining annular space around the drill pipe above the level of the sea floor, and the much greater water depths involved, as well as various other factors. In current DSDP operations, any gas encountered, under pressure sufficient to cause it to enter the hole and permeate the drilling fluid, would, as it travelled upward, be confined only until it reached ocean floor (top of the bore hole), or until it reached the base of such interval of soupy, fluid sediment as might locally lie immediately below the ocean floor. Above this point, the gas, although continuing its upward course, would probably also tend to dissipate away from the vicinity of the bore hole, and would reach the ocean surface, if at all, in less concentration and over an increasingly broad area in proportion to the water depth (thickness of water column) through which it had to pass.

Considering the usually much greater water depths involved in DSDP drilling than in normal oil well drilling, there is relatively much less danger in the former of a violent outbreak of gas at the surface with accompanying hazards to the drilling vessel. However, at the same time, the means of control over the results of a gas flow into the hole are also much less effective under current DSDP operating conditions. It is entirely possible that a blowout could occur even with drilling operations in water depths of 500 m or more. Moreover, even though the escape of gas or oil at the ocean surface from holes drilled in water depths of several thousand meters might be so diffuse as not to be readily discernible, the total pollution of ocean waters by hydrocarbons (or the dissipation of potential hydrocarbon resources) might be as great or even greater than in a more violent blowout. It is even possible that a continuing substantial escape of hydrocarbons into the ocean waters from a DSDP hole could occur so quietly as to completely evade notice from the drilling vessel.

A gas blowout could imperil the vessel and crew in several ways - by release of noxious gases, by fire, or by causing a loss of the vessel's buoyancy due to charging of the surrounding sea water with gas bubbles.

Hydrogen sulphide is the principal highly noxious gas that might be encountered. It has often been found in high concentration in petroleum drilling operations but is easily detected by several commercial devices and is identifiable even in low concentration simply by its characteristic odor.

The greatest fire danger from a gas blowout on the GLOMAR CHALLENGER would occur if a blowout of hydrocarbon gas took place through the drill pipe. However, in relatively shallow water, gas escaping to the surface from around the drill pipe at the sea floor may also present a fire hazard to the vessel. The CHALLENGER drill crews must be trained in the standard oil field practices for avoiding or controlling these possibilities.

Aeration of the sea by gas to the point where buoyancy is seriously impaired could hardly occur in the water depths usually encountered at DSDP sites. However, this has apparently happened twice with vessels drilling for oil in shallow water and the possibility should not be ignored at the shallower DSDP sites.

B. Intercommunication Between Reservoirs and Exchange of Fluids

This situation may occur when formation fluids (oil, gas, water) from deep, high-pressure zones, in process of flowing up the bore hole, pass shallower zones with lower normally-pressured formation fluids. A real danger exists that under these conditions hydrocarbons may enter a zone that opens to the sea floor by outcrop or fracture, resulting in an uncontrollable leak. Furthermore, high-pressure fluids from deep zones may in the same way charge shallow zones with fluids above normal hydrostatic pressure and thus make even shallow future drilling in the area hazardous. Also, it is possible, though not very likely under DSDP conditions, that deep saline formation water might in this way contaminate valuable shallower fresh water aquifers.

C. Political Concerns

Questions of political jurisdiction over areas in which the DSDP is operating may involve hazards due to conflicts between various national claims and due to uncertainties regarding national-international boundaries at sea. Also, different countries may have different standards with respect to pollution prevention. It does not seem appropriate for the Panel to take responsibility for problems of this nature which may arise, since their solution involves international law and top-level policy for the whole program. However, the Panel has requested the Chief Scientist to supply information on distances of sites from shore and probable political jurisdictional control at each site and it has considered that it is its duty to call attention to possible political hazards which might arise. (See Section IV-J.)

D. Other

Hazards of storms, hurricanes, ice, collisions, etc., are common to all vessels and consequently are not detailed here. Likewise, the hazards involved in the mechanical operation of drilling equipment are common to all offshore drilling operations and do not require special mention.

While not detailed here, it is of course mandatory that conventional safety measures used in oil field operations and on drilling vessels, such as safety hats, no smoking except in designated areas, emergency blowout and fire drills, etc., be observed at all times. It is also essential that measures be taken to prevent pollution of the environment by any of the operations incidental to the program.

III. GENERAL OBSERVATIONS ON PRECAUTIONARY MEASURES, RESPONSIBILITIES, INFORMATION REQUIREMENTS, AND PANEL PROCEDURES

Topics considered by the Panel to be the most important to stress for purposes of safety and to prevent hazards to the environment are treated below under the following five heads:

- (1) Choice of reasonably safe drill sites
- (2) Proper planning of the drilling program for each site
- (3) Early detection or anticipation of hydrocarbons or high fluid pressures during drilling
- (4) Measures for coping with flows of fluids encountered or anticipated during drilling
- (5) Measures for abandoning holes

Care in the first of these -- Choice of reasonably safe drill sites -- probably offers the greatest return in insurance against trouble.

The Panel strongly believes that it is the responsibility of those who plan each Leg and its drilling sites (Site Survey Panel) to consider each of these topics, both in advance planning and in connection with shipboard operations. It is also their responsibility to propose to the best of their ability only drilling sites and drilling programs which they themselves can conscientiously support as reasonably safe. The function of the Panel on Pollution-Prevention and Safety is only to check again from the safety angle proposals of sites and drilling programs for the safety of which the planners of the Leg are already willing to take responsibility.

Those who are responsible for initially planning a Leg should do so only after thoroughly considering the possible hazards and the precautions outlined in this Manual and adjusting their proposals accordingly. There should be no attitude of attempting to "run a program by" the Panel or shift responsibility to the Panel for any program for which the original proposers are not also willing to take full safety responsibility. Decisions on risks should be made with the recognition that it is not one site or one Leg that is concerned but the future of the whole program which may be jeopardized by an accident or a pollution incident.

The Chief Scientists of each Leg or the Site Survey Panel should be responsible for presenting to the Panel for Pollution-Prevention and Safety sufficient data to allow a thorough evaluation of each of the above listed safety components for that Leg and for each drill site proposed. Unless adequate data are provided, the Panel must refuse to consider a proposed site or drilling program. Moreover, these data should be provided in time to allow review by individual Panel members

in advance of the meeting at which a Leg is scheduled for review by the Panel. Only definitely identified and supported locations can be approved by the Panel, and if a location approved by the Panel is subsequently moved it cannot be considered to have been supported by the Panel. Further details on information requirements of the Panel and Panel procedures are given in a letter of January 19, 1973 from the Chairman of the Panel to the Chairman of the JOIDES Executive Committee reproduced here in Appendix A.

Once drilling operations are started on a hole, the responsibility for safety and pollution measures, including cessation or abandonment of drilling, should be clearly fixed on the Cruise Operations Manager, who should be thoroughly experienced in the hazards of petroleum drilling. He will, of course, consider the recommendations of the Chief Scientists. Both the Cruise Operations Manager and the Chief Scientists should desirably be present at the Panel meeting held to consider that Leg. Furthermore, it is strongly recommended, on any Leg where the geology of the region is known to be generally conducive to petroleum origin and accumulation, that the scientific personnel on board the vessel include a geologist with a background of experience with petroleum exploration and production wells.

IV. PRECAUTIONS IN CHOICE OF DRILL SITES

A. Thickness and Character of Underlying Rock Strata

It is basic both to the general program and to safety and pollution prevention to make in advance the best possible estimate of the total thickness of the sedimentary section at a proposed drill site and the probable organic content and lithology of the rocks to be penetrated.

Thickness of sedimentary strata above igneous or metamorphic rock basement is one of the most useful factors in initially deciding whether or not the section at a drill site has potential petroleum hazards. It is generally agreed that most petroleum results from thermochemical action on organic matter buried in the sediments and that usually this generation takes place abundantly only after the sediments have been buried to a depth of 1000 m or more so that, as a result of the geothermal gradient, they have reached temperatures of some 50°C or more (see Section II-A-1 and Appendix C-1). It is difficult to predict in advance of drilling whether or not there has been a sufficient supply of organic matter in a section to have allowed substantial petroleum generation, but seismic information can usually provide reasonably accurate advance information on the sedimentary thickness at a proposed drill site. Lacking any definite information on the absence of petroleum source material, thick sedimentary sections (1000 m or more) must always be looked on as possible progenitors of petroleum and should be drilled with appropriate caution.

For purposes of considering petroleum hazards, oceanic areas may in a general way be divided into those with more than 1000 m of sediment above basement (most of the shelves, slopes, and rises adjacent to continents or islands; many of the small ocean basins and oceanic troughs; and some few sediment-filled basins far from land in the main oceans) and those with less than 1000 m of sediment (constituting most of the vast central areas of the major oceans, the mid ocean ridges, and many trenches and local areas nearer to land).

Sedimentary columns less than 1000 m thick in general have not experienced sufficient geothermal heating to have allowed in situ generation of abundant liquid petroleum. Such areas of relatively thin sediments are thus relatively low in oil hazards even where they contain or have contained considerable potential source organic matter, if these areas are so situated that there is little possibility of them having once been more deeply buried, or unless they are at the wedging out margins of adjacent sedimentary basins with thicker columns of potential oil-generating sediments from which lateral migration could have taken place or unless they have experienced greater than normal heat flow as in basins developed over areas of initial sea floor rifting. In general the Panel considers the vast central oceanic areas with only 500 m or less of sediment above basement to be nearly free from petroleum hazards. However, even in such areas consideration must be given to the possibility that thick older sedimentary sections may underlie the present acoustic basement (usually oceanic basalt), and also there is always a possibility of accumulations of biogenic methane.

Obviously, hydrocarbon hazards are greatly increased if there are good potential reservoir strata in the section and this factor has an important modifying bearing on safety conclusions based purely on thickness and probable organic content. Seismic data and regional geologic considerations may give helpful information on the probability of substantial reservoirs being present in a section. Drilling should not be carried into sections showing seismic "bright spots" indicative of gas reservoirs.

The anticipated presence of evaporites, over-pressured shales, clathrate zones, and other sealing lithologies, below which hydrocarbons may be trapped, has an important bearing on the depth to which a drill hole can be carried safely. Likewise, the presence of evaporite or shale diapirs is a danger signal.

B. Structural Attitude and Probability of Trap Features

Equally as pertinent as the thickness-of-sediment factor in evaluating the riskiness of a drilling site is the matter of whether or not the hole is likely to penetrate a trap feature capable of holding hydrocarbons. It is recommended that at least one continuous seismic profile be obtained across any prospective deep sea drilling site and that two intersecting profiles approximately at right angles

be obtained for any prospective drilling location on the shelf, slope, or rise or any other area of potential hydrocarbon accumulation. Features of trap significance to be checked on the seismic profiles include folds, faults, pinchouts, unconformities, diapirs, etc. Any sort of a trap feature (structural or stratigraphic) within the section to be penetrated should be avoided in the choice of drilling locations. While reliance must be placed primarily on seismic sections for the identification of trap features, other available lines of evidence such as gravity, magnetics, and detailed bathymetry may also be helpful.

It often happens that those responsible for picking the drilling locations of a Leg tend to put them at the crests of structural highs because such sites represent minimum drilling distances to stratigraphic objectives. However, these are at the same time the most hazardous places to drill because of the danger that they or their flanks may also represent trapping features for petroleum. It is urged that the Chief Scientists (or Site Survey Panel) in the initial selection of locations seek places off structure where the desired objectives can be reached, even if this means some extra drilling distance.

C. Known Oil and Gas Occurrences

The planners of a Leg should obtain information on all known or suspected oil and/or gas seepages or other hydrocarbon occurrences relevantly close to the proposed sites of that Leg. This is most important with respect to prospective locations on continental margins. Both on-shore and off-shore data are desirable. Petroleum companies who hold or have held acreage in the general vicinity should be consulted. Consideration should be given to making hydrocarbon surveys in the vicinity of proposed sites to sample bottom waters in order to avoid areas of pronounced high hydrocarbon content which might reflect underlying petroleum accumulations. Also, piston cores at proposed sites may yield useful advance information on hydrocarbon concentrations in the surface sediments of these areas.

D. Abnormal Pressures

Areas and section intervals in which fluids are under greater than normal hydrostatic pressure should be avoided as far as possible as they represent hazards to safety because of common association with gas or oil and because of the danger of blowouts.

The presence of undercompacted shale is a warning that fluids will be encountered at more than normal hydrostatic pressure. (An undercompacted shale is one in which fluid expulsion has not reached equilibrium with fluid pressure, so that the formation fluid in the shale, and perhaps in associated sands, is under not only hydrostatic pressure but, in addition, carries also a part of the weight of the overlying rock column and perhaps also some component of internally generated pressure.) Undercompacted shales often may be identified

in advance of drilling by means of velocity inversions or decreases in interval seismic velocity with depth due to abnormally high fluid content. They may also appear as sections with distorted bedding, usually strongly convoluted; or they may show up on gravity profiles because of their lower density. Absence of a velocity inversion does not, of course, preclude abnormal formation pressure, nor does the presence of a velocity inversion always result from an undercompacted shale section. However, drill sites at which marked velocity inversions are detected should be avoided, unless the inversion can be related clearly to simple lithologic change.

E. High Geothermal Gradient

If possible, heat flow data should be acquired at prospective drilling sites because higher than normal temperatures are commonly associated with above-normal pressures and hydrocarbon accumulations.

F. Water Depth

The dangers of oil and gas blowouts to the safety of the vessel and its personnel diminish greatly with increasing depth of water. Thus while violent surface blowouts might occur in water depths as great as 500 m there would appear to be little likelihood of such blowout dangers at 2000 m or more. However, quiet escape of oil or gas into the sea with consequent risk of pollution of ocean waters and loss of valuable hydrocarbon resources can occur while drilling in any water depth.

G. Significance of Clathrates to Safety of Drill Sites

Certain gases; including the light C_1 - C_3 hydrocarbons, H_2S , and CO_2 can combine with water to form a stable solid clathrate (gas hydrate) structure under the low temperatures and high fluid pressures of sediments just below the deep ocean floor. Because of steadily increasing temperature downward below the ocean floor, the clathrate structure is stable only within a limited thickness of the upper part of the sediment column and a critical temperature is soon reached beyond which the clathrates cannot exist in spite of the increasing pressure with depth. The thickness of the potential clathrate zone will vary with water depth, with local bottom water temperatures, with local geothermal gradients, and with composition of the gas, but may commonly extend to the order of several hundred to a thousand meters below the ocean floor. In the sediments above this depth of critical decomposition temperature, any methane in excess of the quantity required to saturate the interstitial water will theoretically be combined with water to form the solid clathrate. Below this critical

depth solid gas hydrates will not be formed, and those which may have been formed at shallower depth will melt as deposition and subsidence, or deposition alone, bring them below this point.

Small quantities of CO_2 , ethane and propane have a stabilizing effect on the clathrate structure while increased salinity has a destabilizing effect. In deep sea sediments these effects approximately cancel each other, so that the best available estimates of clathrate stability are given by experimental work on the system pure CH_4 -pure H_2O .

The phenomenon of methane clathrate formation provides both a safety factor and a hazard in DSDP drilling. Over much of the ocean area at water depths greater than 1000-1500 meters excess methane present in the sediments of the ocean floor will have been immobilized in the form of a clathrate and thus may be drilled without danger. (Although drilling operations may produce local temperature changes which will release some of this gas into the hole, it seems probable that such release will be so narrowly limited to the immediate proximity of the hole that there will be little possibility of any substantial gas escape or gas blowout.) However, below the critical depth in the sub-ocean strata at which methane clathrate can exist, which may be on the order of several hundred to a thousand meters depending on the geothermal gradient, reservoir rocks beneath a clathrate zone may be filled with gas in large volume and at high pressure, trapped below the seal of the overlying clathrate. Moreover, such trapping may occur not only on geologic structures but also in flat-lying beds, merely due to irregularities in the lower surface of the clathrate zone. Where previously formed clathrates have melted at the base of the clathrate zone, dangerous high-pressure gas accumulations might particularly be expected.

In view of these considerations and considering the limited pressure control equipment of the GLOMAR CHALLENGER, it should be a rule that drilling should never be carried into the strata underlying the potential clathrate zone in a section where there is a prospect of the occurrence of methane and the presence of reservoir strata. For each hole where penetration of more than 100 meters is planned, calculations should be made, based on bottom water temperatures, overburden pressures (water and rock), and probable geothermal gradient, to show the supposed upper and lower limits of the theoretical methane clathrate zone; and the drilling program should be adjusted accordingly.

Although drilling within the clathrate zone may be safe with respect to "non-associated" gas blowouts or gas escape, it should be borne in mind that the clathrate phenomenon does not apply to liquid hydrocarbons. Even within the sealing clathrate zone, the normal dangers of oil leaks and oil and solution gas blowouts persist wherever there are possibilities of encountering oil accumulations. Also it is of course conceivable that a gas accumulation formed previous to clathrate conditions may still persist although now surrounded by sediments with clathrated gas.

Direct observation of clathrates in natural sediments is still meager although, because of the increased velocity of transmission of seismic waves in clathrate-filled sediments as compared to fluid-filled sediments, probable clathrate horizons can often be picked up on seismic profiles as horizons related to depth below the sea floor but independent of the structural attitude of the rock strata. (See Lancelot and Ewing, 1972, Figure-2, p. 793, for an example.) Likewise a few cores of natural clathrates have been recovered on land by use of a pressure core barrel and attempts are being made to utilize a pressure core barrel on the GLOMAR CHALLENGER to recover clathrates from below the ocean bottom. It seems probable that much new information on clathrate occurrence will be developed in the next few years. It is recommended that DSDP sponsor the drawing up of some pertinent guide charts based on available pressure and temperature data to show the probable distribution and depth range of the clathrate zone in specific geographic areas where DSDP holes are planned. This Panel has asked the JOIDES Panel on Organic Geochemistry to undertake this work.

Among pertinent literature references on clathrates are several articles by various authors in Natural Gases in Marine Sediments (Ed. I. R. Kaplan), Plenum Press, New York, 1974. Also see:

Stoll, R.D., J. Ewing and G. Bryan in Jour. Geophys. Res., v. 76, no. 8, pp. 2090-2094, 1971.

Lancelot, Y. and J.I. Ewing, in Initial Reports of the Deep Sea Drilling Project, v. 11, pp. 791-799, 1972. (Shows seismic profile with clathrate reflector cutting across bedding planes on Blake-Bahama Outer Ridge.)

Claypool, G.E., B.J. Presley and I.R. Kaplan in Initial Reports of the Deep Sea Drilling Project, v. 19, pp. 879-894, 1973.

R.D. McIver in Proc. Ninth World Petroleum Congress (Tokyo) v. 2, 1975 (in press).

The possible significance of the clathrate phenomenon to safety aspects of the DSDP was discussed in a memorandum of October 17, 1974, to the Panel from its Chairman, which is included here as Appendix B.

H. Weather

Acquisition of data on weather conditions throughout the year is essential for choosing the optimum season for drilling in a particular area. It is recommended that the Chief Scientist (and Site Selection Panel) become familiar with anticipated weather and sea conditions at the sites of a proposed leg so that timing can be adjusted to minimize hazards which might occur because of weather, or the need for abrupt termination of drilling due to anticipated weather. In high latitudes, information on ice conditions will of course be an important safety consideration.

J. Political Considerations

In general, the nearer a site is to shore the greater the need for precautions against pollution. The offshore jurisdictional claims of different coastal nations are quite variable and the waters adjacent to their coasts may be subject to varying regulations by these nations. Therefore it is recommended that the distance from shore and the jurisdictional claims of adjacent coastal states be thoroughly reviewed in advance by the Chief Scientist (or Site Selection Panel) on each Leg.

While it does not seem appropriate for the Panel to take responsibility for recommendations on these problems, it does appear desirable for the Panel to call attention to their existence and the need for their handling by the proper parties.

V. PRECAUTIONS IN PLANNING DRILLING PROGRAMS FOR INDIVIDUAL HOLES

A. Depth of Penetration

In general, a penetration to no more than 50 m of section, even on top of a structure, is not hazardous since a high pressure hydrocarbon accumulation would be most unlikely at such shallow depths. However, any deeper penetration should depend on the assurance with which the absence of a dangerous combination of hydrocarbon sources, trap structures, and potential reservoirs can be established.

B. Coring Program

The only means currently available to DSDP for detecting an occurrence of hydrocarbons in a drilling hole, short of an actual blowout, is through the examination of cores and drilling fluid obtained from the hole. In holes where the risk of occurrence of hydrocarbon reservoirs is relatively high, it is recommended that coring be done continuously. Other sites may require, as a minimum, coring at specific intervals. It is recommended particularly that cores be obtained at depths where a marked change in drilling rate occurs.

C. Well-Logging Program

It is considered desirable that all holes on the shelf and slope, or wherever thick potentially petroleum-bearing sediments are to be drilled, be surveyed by electrical, sonic, or nuclear logging. This should help in the identification of reservoirs where an exchange of fluids might occur, in the identification of undercompacted shales and in the location of hydrocarbon-bearing formations. In addition, it should be of value in the formulation of a protection or plugging program. Sidewall sampling following logging may help to check features indicated by the logs. It is particularly important that on thick-sedimentary-section holes scheduled for re-entry, logs be obtained at each stage before re-entry.

D. Re-entry

The greater depths of penetration that can now be achieved since re-entry capability became available to DSDP will obviously increase the chance of encountering hydrocarbon reservoirs and the risks of blowouts. However, the re-entry capability may also be of value in aiding pollution-prevention and safety, since, for example, it provides a means of checking cement plug jobs and since it facilitates the utilization of well logs before reaching final depth in a hole.

VI. MEASURES FOR EARLY DETECTION OR ANTICIPATION OF HYDROCARBONS DURING DRILLING

A. Prompt Examination of All Cores and Samples of Drilling Fluid for Shows of Oil or Gas

Every new DSDP hole drilled is to a large extent a venture into the unknown, no matter how carefully the site was picked and the drilling program planned, or how assured its prognosis seems to be. If it were not a venture into the unknown, there would be no point in drilling the hole. Constant vigilance with regard to detection of hydrocarbons and the approach to hydrocarbon accumulations should be observed throughout the drilling of every site where such accumulations are a possibility. Moreover, as stated in Section III, "it is strongly recommended, on any leg where the geology of the region is known to be generally favorable for petroleum origin and accumulation, that the scientific personnel on board the vessel include a geologist with a background of experience with petroleum exploration and production drilling."

Routinely, a visual examination should be made of each core as soon as it is removed from the barrel. Visible oil-staining should call for immediate cessation of drilling, at least until the situation can be appraised thoroughly by those responsible on board. A designated responsible member of the scientific party should promptly examine all cores and fluid recovery for obvious hydrocarbon shows, and those which

appear possibly significant should be analyzed immediately by suitably qualified personnel. In addition, appropriate samples should be selected and examined for solvent cuts and for fluorescence under ultra-violet light. (It should be recognized that hydrocarbon gas and some light liquid oils and condensates can fill a reservoir rock without there being visible staining.)

Samples of drilling fluid from the bottom of the hole may be even more significant than examination of the recovered cores as to whether or not the hole has been drilled through sediments containing hydrocarbon accumulations. When most cores are pulled some drilling fluid, probably from the bottom of the hole, is found trapped in the inner core barrel. This fluid should always be examined for hydrocarbons.

The principal information to be sought promptly from the examination of samples from the drill hole for hydrocarbons is: (1) have hydrocarbon-bearing strata been penetrated that may be polluting ocean waters or adjacent strata or causing a hazard to safety? and (2) what warning signals of an approach to danger can be found which, as regards safety and pollution-prevention, may bear on the advisability of discontinuing drilling? The significance of hydrocarbon shows with respect to these questions is obviously very great, but can be evaluated properly only in the light of many other factors such as the general geologic background of the region, the probable lithologic and lithogenetic character of the section penetrated and to be penetrated, petroleum indications elsewhere in the region, the records of other holes drilled in the vicinity, the probability of encountering reservoir rocks, the probability of source rocks, the probability of evaporites or under-compacted shales in the section, the probable temperature-pressure conditions with respect to clathrate formation, the probability of structural or stratigraphic traps, the water depth, the proposed drilling and coring program, the objectives of the hole, and so on.

Probably the best guideline that can be given is simply that drilling should be stopped immediately whenever hydrocarbons or hydrocarbon indications are encountered under circumstances which suggest the presence of, or proximity to, substantial accumulations of either hydrocarbon gas or oil.

There are several features of the chemical composition of the hydrocarbons detectable in cores or samples of drilling fluid that may contribute importantly to a proper understanding of the situation, on the basis of which an intelligent decision can be made. Although no one of these by itself provides the basis for any hard and fast rule for deciding when a hole should be stopped, they are so significant that the acquisition of such geochemical information from all samples is strongly urged.

The identification and determination of the chemical and physical properties of any liquid or solid petroleum or petroleum-like substances will, of course, be critically important with respect to whether dangerous accumulations have been encountered or may be imminently expected. The chromatographic determination of the amounts and ratios of low-carbon-number paraffins in any hydrocarbon gas shows may be of helpful significance in distinguishing hydrocarbon gases of biogenic origin (or other origin not associated with oil), from hydrocarbon gases which have leaked from some underlying oil and gas accumulation. Gases which have been associated with liquid petroleum commonly have ethane contents of several percent of the total hydrocarbon component of the gas phase, with relative amounts of heavier hydrocarbons (C_2 to C_{13}) decreasing in proportion to their vapor pressure. Gases of this composition were encountered in DSDP Hole-2 of Leg-1 and in Hole-88 of Leg-10. (A detailed discussion of the interpretation of gas shows based on past DSDP experience is given in Appendix C-2.)

Between this extreme and the more frequent occurrence in DSDP holes of gas consisting of methane as the only hydrocarbon detectable by thermal conductivity-gas chromatography, there have been sediment gas shows in DSDP holes in which the methane is accompanied by very small but significant quantities of ethane (C_2/C_1 on the order of 10^{-6} to 10^{-3}). In many of these cases the relative ethane content has shown increases in an erratic but overall exponential fashion with increasing depth of penetration and appears to be due to some very slow in situ generation of ethane by thermochemical processes, increasing with depth and beginning at relatively low near-surface temperatures. Some also have postulated that under certain conditions bacteria may have been capable of generating minor amounts of ethane. In any case, it should be emphasized that it is primarily the quantity of hydrocarbon gas and the possibilities of accumulation and trapping that pose the potential danger, not the origin or composition, important as are these latter for an understanding of the nature of the occurrence. Also it should be emphasized that some of the largest known accumulations of hydrocarbon gas of thermochemical origin are not associated with oil and have an extremely low content of ethane and heavier hydrocarbons, presumably due to the type of organic matter from which they originated. Sections with organic matter consisting exclusively of lignite and carbonaceous shale generally produce gas only -- methane, with only a very low content of ethane, if any.

Because the degree of generation of petroleum liquids and gases from organic source rocks is closely related to the temperatures which these source rocks have experienced, it is important to determine the stages of temperature alteration (maturation) which the organic matter in DSDP samples have attained. This may be ascertained not only from the chemical composition of sediment gas and the nature of solvent-extractable hydrocarbon constituents but also by coloration and reflectance of detrital organic particles and by other means. Various maturation characteristics of organic matter are discussed in more detail by George Claypool in Appendix C-1.

It is difficult to find reliable means for calculating the quantitative values of hydrocarbons in shows in DSDP samples, particularly because the degree of dilution of hydrocarbons in the material examined is difficult to know. A rough method of estimation based on core expansion is discussed by George Claypool in Appendix C-3. The significance of degrees of mud expansion (suggesting approach to pore water saturation), is that gas migration and accumulation can occur when this condition is fulfilled, provided other geologic prerequisites are also met. However, it must be recognized that quantitative figures will vary greatly with rock porosity and permeability and other factors and that the principal hazards may lie in the unknown rocks just ahead of the drill rather than in the section already penetrated.

It should be kept in mind that the nature of hazards indicated by gas content of DSDP samples may be considerably modified if the interval of potential clathrate formation can be established for the site in question, as discussed in Section IV-G. The position of this interval may be estimated from data on pressure, temperature and geothermal gradient. Confirmation of clathrate occurrence should be possible on the GLOMAR CHALLENGER by means of a pressure core-barrel, the use of which is now being perfected.

In connection with work on board the GLOMAR CHALLENGER on hydrocarbon shows, it is urged that the presently used instrument for detecting fluorescence be replaced by more sophisticated equipment that will allow more quantitative discrimination in the interpretation of readings. It is also urged that the present gas chromatograph be replaced by a more effective instrument, such as is used on industry vessels, capable of identifying a broader range of hydrocarbons. Work should be continued toward perfecting the use of the pressure core-barrel for clathrate identification and a series of charts showing the anticipated clathrate range in various regions for prospective drilling should be prepared. (12-15-75 -- It is understood that action has already or will be taken promptly on all these points.)

B. Identification of Cap Rocks, Undercompacted Shales, Clathrates, Sulphur, Evaporites, Reservoirs, Source Rocks, etc.

All of these constitute warnings of conditions which could be favorable for substantial accumulations of hydrocarbons or of non-hydrocarbon fluids. It is recommended that drilling stop on encountering cap rock and be continued only with great caution in undercompacted shales and evaporites, or if sulphur is encountered. With respect to undercompacted shale, an apparatus for determination of bulk density is now included in the ship's laboratory. It is recommended that a technician on each leg should be trained in its use. The measurement of bulk density as a clue to undercompacted shales should take into consideration the fact that considerable depth of penetration is necessary to establish a reliable gradient for normal compaction in any area, and CaCO_3 cementation or other lithologic deviations from pure shale will complicate the interpretation of results. Once a hole has been

completed a sonic or density well log would provide a means of identifying an undercompacted interval due to its lower than normal velocity and density. Also a reversal in the trend of the "shale line" with depth on electrical resistivity logs is commonly significant of an undercompacted shale interval.

Prompt determination of the general lithology of cores is of course important in many ways for safety and pollution-prevention purposes.

C. Continuous Observation of Drilling Rate

The drilling parameters, including meters penetrated, which determine rate of penetration are continuously recorded. This recorder should be monitored for drilling rate changes which might indicate potential hazards. A sudden increase in drilling rate is commonly a warning of entry into an undercompacted shale, which may presage conditions favorable to hydrocarbon trapping.

D. Monitoring of Precision Echo Sounder or PDR

Monitoring of the precision echo sounder or PDR, in order to detect escaping oil or gas bubbles, has been suggested as a safety precaution, although it is to some extent impracticable while drilling, because the PDR pulse is displayed on the positioning system oscilloscope superimposed on the beacon pulse which is somewhat confusing to the operator.

E. Bottom-Hole Temperature and Pressure Determinations

To a certain extent, hydrocarbon accumulations have been noted to be associated with abnormal temperature gradients. With a bottom-hole heat flow measuring device available, it should be possible to pick up warning temperature gradient anomalies. The pressure core barrel which is currently being tested should be useful for confirming the presence of over-pressured shales as well as clathrates (see IV-G and VI-A).

F. Well-Logging

Thus far little use has been made of electrical or other automatically recorded well logs on the DSDP holes. However, these should add greatly to the useful information obtained from the program and would constitute invaluable scientific records of the holes for future reference, in addition to being of value with respect to pollution-prevention and safety through help in the identification of reservoir and sealing rocks, undercompacted shales, detection of hydrocarbons, and determination of the character of fluids filling the pore spaces of rocks penetrated. The running of well logs from time to time in a hole may be very helpful in determining how deep a hole can be carried with safety.

One of the principal values of the mechanically recorded well log (electrical, sonic, or other) is that it provides a continuous record of the hole through intervals that were drilled without coring and through intervals where core recovery was poor. With the advent of the IPOD Program and the probable increase in the number of holes where change of bits and re-entry will be required to attain objective depths, it seems highly essential for safety and pollution-prevention purposes as well as for other reasons to have a well-logging capability on board and to log each stage of penetration before going back into the hole. Such logs will provide one of the most unequivocal means of detecting oil and gas reservoirs in the section, and should be a "must" for holes requiring deep penetration into thick potentially hydrocarbon generating sedimentary sections.

G. Monitoring of Fluid Coming up Around the Drillstem

Until a riser system to allow circulation of drilling fluid can be put into operation, DSDP drilling must be at a distinct disadvantage with respect to safety and pollution monitoring as compared with conventional oil well drilling operations because of the lack of a continuous record, brought to the deck of the vessel by the drilling fluid, of the rocks penetrated and the fluids coming into the hole. Several alternatives have been suggested.

A report of March 11, 1971 (with supplementary letter of April 13th) by R.D. Townsend, Jr. entitled "Investigation of Pressure Control Systems for DSDP Operations" discusses the possible use of airlift induced reverse circulation of sea water and formation cuttings up the drillstring, together with downhole blowout preventers in the drill string. This system as described would involve a dual coaxial drillstring, air compression equipment, etc., at an estimated cost of \$900,000. It would presumably provide an effective but possibly very dangerous means of monitoring oil and gas occurrences in the sediments drilled.

A much simpler, possibly almost equally effective, and certainly much safer alternative would be to devise apparatus whereby a continuous water stream could be pumped to the surface from the sea floor in close proximity to the point of entry of the drillstem and monitored on board for hydrocarbon content (Letter of August 29, 1975, HDH to N. Terry Edgar). Such a device would provide an important continuous check on the hydrocarbon content of the drilling fluid coming out of the hole at the sea floor and thus a rough check on the hydrocarbon content of formations penetrated by the bit. If the water pumped to the surface showed little indication of hydrocarbons it could be reasonably assumed that no pollution of the ocean was taking place. Consideration might also be given to the use of such a device for sampling the bottom waters above a proposed drill site before drilling as an abnormally high hydrocarbon content might serve as a warning against such a site.

Another suggestion for monitoring the drilling fluid at the ocean floor as it comes from the hole is to use a "pinger" which would acoustically detect gas bubbles.

VII. MEASURES FOR COPING WITH FLUID FLOWS ENCOUNTERED OR ANTICIPATED DURING DRILLING

A. Use of Heavy Mud

In current DSDP operations, the drilling fluid (normally sea water) cannot be circulated. Drilling mud, when spotted, is displaced from the hole if drilling or coring is resumed. 400 to 500 barrels of weighted mud should be kept mixed at all times to be used to kill any tendency for fluid flow up the drill pipe and for plugging purposes.

Attention has been called to the successful use of spotting barite plugs to kill wells threatening to flow out of control. "The plug, mixed to weigh 18-20 lbs. per gallon, will, under certain applications, offer the better features of either cement or heavy mud. It can be kept on hand mixed and continuously stirred ready to pump. When it is in place, a 200-400 ft. column will offer considerable overbalance to control the well. It will not "honeycomb" with gas and remain permeable to small seepage leaks like cement is inclined to do under some conditions, and if desired, it can be washed out to reopen the hole." -- Letter of January 6, 1971 from J.H. Norman to H.R. Gould of Esso Production Research Company. We strongly recommend the use of the barite plug method for emergency control in DSDP drilling.

B. Use of Moderation in Coming Out of the Hole to Avoid Swabbing Effect

This is not normally a problem on the CHALLENGER. Drillstring lengths are such that coming out of the hole is almost always slow. However, the driller should watch the weight indicator carefully for the first few stands to detect balled-up bits. Care should be used in pulling the wire line core barrel.

C. Considerations with Respect to Use of Blowout Preventers

The use of conventional blowout preventers in the DSDP to date has not been possible due to the absence of riser pipe. However, the use of an "in-the-string" down-hole pack-off type of blowout preventer was suggested as a possibility by both Gulf and Humble consultants.

"The device referred to is capable of being set in open hole provided the hole is not washed out too greatly. A pump-down plug with wireline fishing neck is used to set the packer and this opens circulating ports above the packer. By using a safety joint or "back-off," cement could be placed above the packer and the hole abandoned. A second plug with fishing neck can be pumped down to release the packer and re-establish circulation through the bit in the event heavy mud kills the well and drilling is to be resumed.

An additional safety feature for consideration is the use of a seating groove above the bit, a pump-down back pressure valve, and safety joint. In event pipe became stuck and the annulus packed off, as sometimes happens, the plug could be placed, pipe backed off, cement spotted, and the hole safely abandoned. This is most needed without the down-hole preventer, but might be useful in conjunction in certain cases." -- Comments from Gulf Research and Development Company transmitted by Mr. J. O. Rundle, January 21, 1971.

A downhole blowout preventer of a type which might be utilized is described by Lester L. Cain of Drilling Well Control, Inc., of Houston in "The Drilling Contractor," November-December 1970, pp. 31-34.

Such devices are currently available and it was recommended that attention be given to equipping the CHALLENGER with some type of "in-the-string" down-hole blowout preventer. However, the workability of such a device in poorly consolidated sediments at great water depths might be questionable.

D. Early Abandonment and Plugging

If hydrocarbons are detected under conditions suggestive of substantial accumulations or imminent approach to such accumulations (see VI-A), it is recommended that drilling be stopped and that the hole immediately be plugged with cement or barite to the shallowest competent horizon and filled with heavy mud to the surface.

VIII. SAFETY MEASURES WITH RESPECT TO ABANDONING HOLES

A. Standard Procedures

The following is recommended as standard abandonment procedure:

1. All holes or parts of holes drilled in consolidated¹ or semi-consolidated sediments which are on the shelf, slope, or continental rise, or in which shows of oil or gas are encountered, should be plugged with cement (or barite) to the uppermost competent layer before abandonment. Consideration should be given to the possible advantages of substituting barite plugs for cement plugs (see Art. V-A).

VII-A

¹ The terms "consolidated," "semi-consolidated," and "unconsolidated" with reference to sediments are, of course, relative and difficult to define quantitatively. For purposes of this section of the report, unconsolidated sediments are those which tend to behave like fluids during drilling and completion operations. Semi-consolidated sediments are solids but are highly incompetent under stresses involved in drilling and completion operations. Consolidated sediments are not readily deformed by flow during drilling and completion operations. The terms are not amenable to strict definition.

2. All holes or parts of holes drilled in unconsolidated sediments on the shelf, slope, or continental rise, and all other holes in unconsolidated sediments in which shows of oil or gas are encountered, should be filled with heavy mud before abandoning.
3. Holes in the deep ocean beyond the continental margin in unconsolidated sediments in which no shows of oil or gas are encountered, or holes in igneous rocks, may be abandoned without plugging.

B. Special Procedures

Special conditions may call for variations in the standard procedure outlined above. For instance, in some cases it may be adequate to fill the hole with heavy mud to a certain point and then spot a cement plug above the heavy mud.

IX. MEMBERSHIP OF JOIDES ADVISORY PANEL ON POLLUTION-PREVENTION & SAFETY (as of February 1976)

CLAYPOOL, George, U.S. Geological Survey, Denver
 CURRAY, Joseph R. (ex-officio), Scripps Institution of Oceanography.
 Chairman, JOIDES Advisory Panel on Ocean Margin (Passive)
 EWING, John (ex-officio), Woods Hole Oceanographic Institution. Chairman
 JOIDES Planning Committee.
 GARRISON, Louis E., U.S. Geological Survey, Corpus Christi
 GOODELL, H. Grant, University of Virginia
 GREEN, Arthur R., Exxon Production Research Company, Houston
 HEDBERG, Hollis D. (Chairman), Princeton University
 MAYER-GURR, Alfred, Hannover, F.G.R. (subject to acceptance of invitation)
 REDERON, Christian, TOTAL Oil, France (subject to acceptance of invitation)
 TALWANI, Manik (ex-officio), Lamont-Doherty Geological Observatory.
 Chairman, JOIDES Executive Committee.
 UYEDA, Seiya (ex-officio), Earthquake Research Institute. Chairman,
 JOIDES Advisory Panel on Ocean Margin (Active).
 WESER, Oscar E. (Secretary), DSDP, Scripps Institution of Oceanography
 WINTERER, E.L. (ex-officio), Scripps Institution of Oceanography.
 Chairman, JOIDES Advisory Panel on Site Surveying.



JOIDES JOINT OCEANOGRAPHIC INSTITUTIONS DEEP EARTH SAMPLING

January 18, 1973

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Dr. William A. Mierenberg
Chairman, JOIDES Executive Committee
Scripps Institution of Oceanography
University of California at San Diego
La Jolla, CA 92038

Dear Dr. Mierenberg:

The DSDP Panel on Pollution Prevention and Safety is continually concerned with the objective of keeping DSDP operations reasonably safe and free from blame with respect to pollution and other hazards, while at the same time allowing the maximum in scientific results to be obtained.

The Panel has been particularly reluctant to withhold endorsement of drilling sites when such action may risk disturbing at the last moment a long-planned program of holes. Likewise, it has been reluctant to recommend precautions which might slow down or delay the progress of drilling programs. At the same time, it feels in duty bound to make a conscientious evaluation of the hazards involved in each site and to recommend the precautions which it thinks should be taken if the site is to be drilled.

In order to help avoid, as far as possible, unnecessary last-moment disarrangements or delays in drilling programs on account of Panel actions, the following suggestions are made:

(1) It is essential that the Panel receive the program, proposed site locations, filled-in check sheets, and supporting geophysical data in time for consideration at least several weeks in advance of the starting of a leg. It should be the responsibility of the chief scientist to see that the check-sheets for each site are filled out carefully and with adequate data. He should also prepare for the Panel a brief written description of the structure and stratigraphy to be anticipated at each site and should make certain that members of the Panel are provided with legible prints of seismic data available at each site showing clearly the relation of the proposed site to these data. The Panel should not be asked (nor should it attempt) to pass judgment on sites unless adequate data are made available to it, and in adequate time to allow thorough consideration.

(2) It would be helpful if chief scientists and others concerned with the planning of DSDP legs would read over the Panel's Manual on

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Pollution Prevention and Safety in advance and take the recommendations in this Manual into serious consideration in laying out detailed plans for the sites to be drilled.

(3) It should be recognized by chief scientists, and others concerned with the planning of programs, that areas underlain by 1000 m or more of sediments (or even much less at the uptilted margins of sediment accumulations of this or greater thickness) may commonly contain petroleum accumulations if local trapping conditions are present. Sites in such areas on continental or insular shelves, where water depths are shallow, are particularly hazardous for drilling, considering the equipment presently available on the Glomar Challenger. It is recommended that such sites be designated for drilling only if adequate intersecting seismic lines at the site show no evidence of trap structure (anticlinal closure, unconformity bevel, or other), or unless drilling is made contingent on such structures not being shown by adequate additional seismic work to be carried out at the site before drilling. If, in spite of structural hazards, it is decided to drill such sites, it is recommended that penetration be limited to 200-300 meters and that continuous or nearly continuous coring be carried out below 100 m in order to spot warnings of hydrocarbon accumulation.

(4) Obviously, from time to time, unanticipated events may make it desirable to ask the Panel for emergency advice during the course of a Leg. Where there is time to do so, the Panel members should be consulted by telephone, by mail, or through special meetings for an official opinion. If there is not time for this, individual members of the Panel may be asked for advice but this will be given on an unofficial basis only.

(5) The Panel may sometimes term a certain general area as hazardous or very hazardous for drilling, although not wishing to go so far as to withhold its approval of specific drilling sites in the area, provided specified precautions are taken. (The Ross Sea shelf is a current example). It is understandable that in some cases the DSDP Executive may prefer not to go into such areas at all because of the heightened risks indicated by the Panel or because of the delay and expense necessary in order to take the Panel's prescribed precautions. Likewise it is understandable that the DSDP Executive may in some cases decide that the importance of getting information in such areas, and getting it expeditiously, is so great as to justify overriding the Panel's prescribed precautions even though this means taking greater than normal risks. Similarly, the ship's party may on occasion find the precautions prescribed by the panel so onerous as to lead them to appeal for relaxation. Decisions on these matters and on such appeals are, of course, the

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Dr. William A. Nierenberg

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January 19, 1973

responsibility of the DSDP Executive and not of the Panel, unless new information has been developed which justifies a review by the Panel of its previous recommendations.

Yours sincerely,

(signed) Hollis Hedberg

HDH:ejb

cc: Dr. Wm.W. Hay, Chairman
DSDP Planning Committee

(On behalf of the Members of
the Panel)
Hollis D. Hedberg, Chairman of
DSDP Panel on Pollution
Prevention and Safety

APPENDIX A

JOIDES
JOINT OCEANOGRAPHIC INSTITUTIONS
DEEP EARTH SAMPLING

116 Library Place
Princeton, NJ 08540

October 17, 1974

To: Members of JOIDES Advisory Panel on Pollution Prevention
and Safety:

William F. Allinder
John Ewing
Louis E. Garrison
N. Grant Goodell

Dennis E. Hayes
John Sherborne
Manik Talwani
Edward L. Winterer
Oscar E. Weser (Secretary)

Gentlemen:

In our Manual on Pollution Prevention and Safety in connection with the JOIDES Deep Sea Drilling Program (DSDP), 2nd edition, 1972, we have discussed briefly the importance of solid gas hydrates (clathrates) with respect to DSDP operations (pp. 11-12). A report by a special JOIDES clathrate committee, mentioned in the Manual, is still awaited. However, since the date of the Manual much attention has been given to clathrate formation in sediments, numerous papers have been published, and we should review the significance of clathrates to the decisions of our Panel and perhaps consider amplifying the statement in the Manual.

Direct verifying observation of clathrates in natural sediments is still meager. (I understand that Exxon has recovered two cores of solid methane hydrate from Arctic America with a new pressure-temperature core barrel, but I do not believe this has yet been tried in the deep ocean.) However, it appears to be the conclusion, of those geochemists who have expressed themselves, that methane gas in deep sea sediments exists in the clathrate form within the temperature and pressure range indicated on the accompanying chart (Figure 1, from Katz, 1971). Thus, over most of the ocean floor at water depths greater than 1000-1500 meters any methane present will have been immobilized in the form of a gas hydrate. Although drilling operations may produce local temperature changes which will release some of this gas into the hole, it seems probable that such release will be so narrowly limited to the immediate proximity of the hole that there is little danger of any substantial gas escape or gas blowout. Consequently, there seems little reason for restricting DSDP drilling in deep water within the assured clathrate zone, merely because of a methane hazard.

APPENDIX B

However, with increasing depth below the ocean floor, because of the earth's thermal gradient, rock temperatures are rapidly attained at which clathrates cannot exist in spite of water-column and rock-overburden pressures. (See Figure 2 after Katz, 1971, for an example of the intersection of a gas hydrate curve with the geothermal gradient, Cape Simpson, Alaska.) Below this critical depth which, varying with the local geothermal gradient and the bottom temperature might commonly be on the order of several hundred to a thousand meters below the ocean floor, solid gas hydrates will not be formed; and those which may have been formed at shallower depths will melt as deposition and subsidence, or deposition alone, brings them into this zone (See Figure 3 after Bryan, Ewing and Stoll, 1971). The "base of clathrate" thus becomes a critically important horizon, because below this depth reservoir rocks may be filled with gas at high pressure and large volume, trapped below the seal of the overlying clathrate zone. Moreover, such trapping may occur not only on geologic structures but in flat-lying beds, merely due to irregularities in the lower surface of the clathrate zone. The great volume change resulting from the melting of clathrates could be expected to provide high-pressure accumulations.

In view of these considerations and considering the present limited operational equipment of the Glomar Challenger, it should be a rule that drilling should never be carried into this sub-clathrate zone in a sedimentary section where there is a prospect of the occurrence of methane and of the presence of reservoirs. For each hole where penetration of more than 100 meters is planned, calculations should be made, based on bottom-water temperatures, overburden-pressures (water and rock) and probable geothermal gradient, to show the supposed upper and lower limits of the theoretical methane-hydrate zone; and the drilling program should be adjusted accordingly.

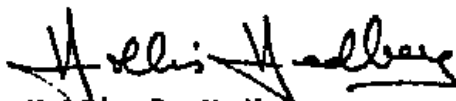
Although drilling within the clathrate zone may be safe with respect to gas blowouts, it should be borne in mind that the clathrate phenomenon does not apply to liquid oil. Even within the sealing clathrate zone, a danger of oil leaks or blowouts due to drilling may still exist wherever there are possibilities of oil accumulations, and the drilling program will need to be adjusted to the oil hazard in addition to the gas hazard. In this connection, however, it might be advisable to stress in the Manual that there is a current consensus that, except in areas of high heat flow, sedimentary columns in the deep oceans which are less than 1000 meters thick have not experienced enough temperature to have caused the in situ generation of substantial quantities of liquid petroleum. Hence in Glomar Challenger operations the oil hazard generally may be considered negligible in deep ocean

October 17, 1974

sections of less than 1000 meters thickness, if these are so situated that there is little possibility that they have ever been more deeply buried, or that oil may have migrated into them from elsewhere.

It is recommended that DSDP sponsor the drawing up of some pertinent guide charts to show the probable relation of the clathrate zone to (1) pressure converted to water depths, (2) to ocean floor temperatures, and (3) to geothermal gradients. Perhaps the Panel on Organic Geochemistry could assist in providing such charts. Also a chart of isotherms at the ocean bottom would be very useful.

Yours sincerely,



Hollis D. Hedberg
Chairman of JOIDES Panel on
Pollution Prevention and Safety

HDH:ejs

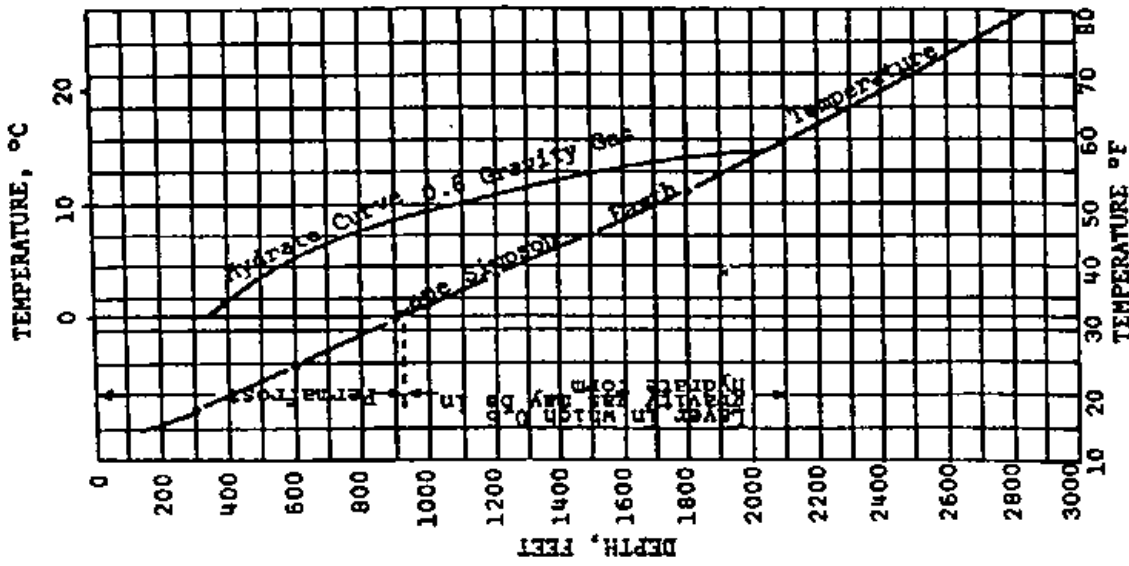


Fig. 2. Method for locating the thickness of hydrate layer. Cape Simpson, Alaska

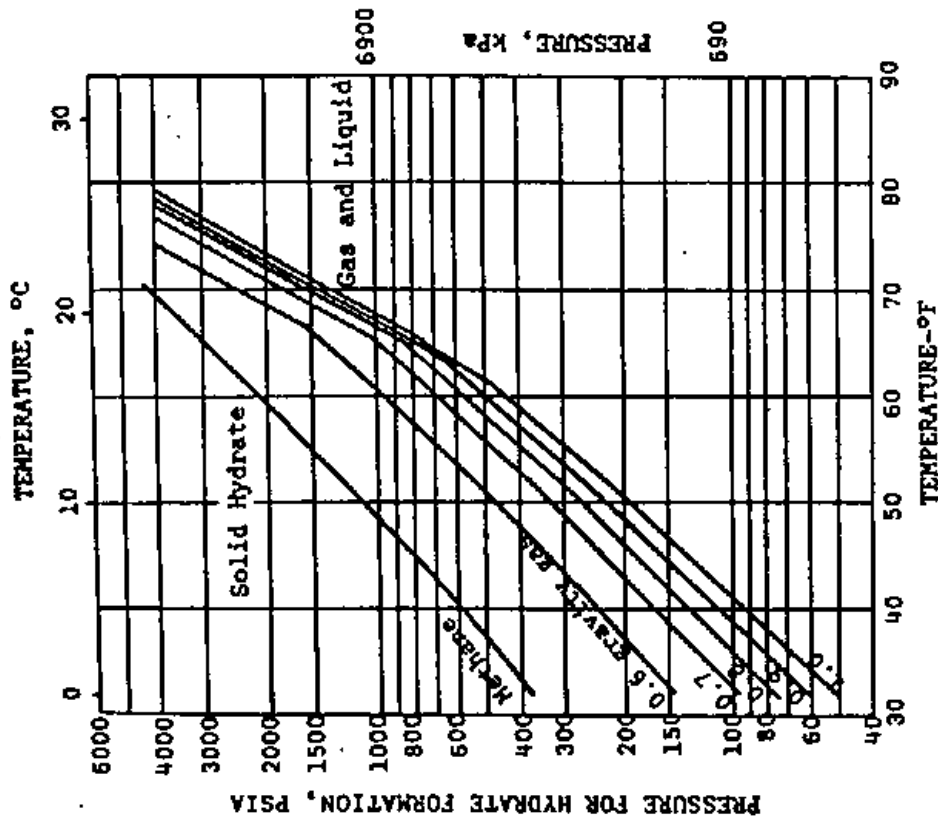


Fig. 1. Conditions for formation of gas hydrates when water is present.

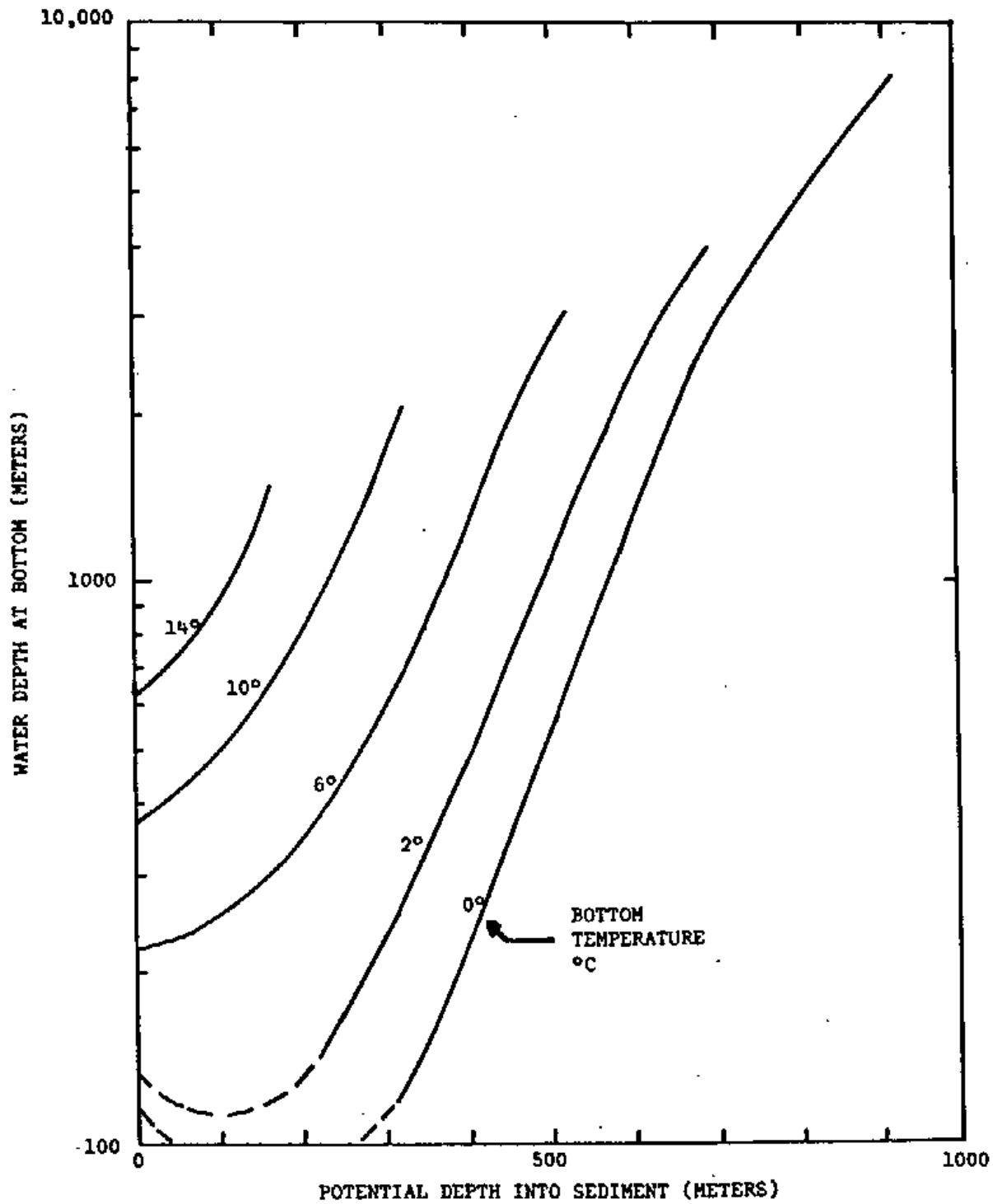


Fig. 3. Maximum potential depths of hydrate formation in sediments.

APPENDIX C

1. Thermal Maturity of Sedimentary Organic Matter: Measurement and Interpretation

Sedimentary organic matter undergoes irreversible thermochemical transformation in response to burial metamorphism. The progress of this time-and-temperature induced transformation can be estimated from physical and chemical properties of the organic matter, or by the relative amounts of organic compounds or fractions which are products, reactants or intermediates in the transformation process. From the standpoint of application in the DSDP/IPOD program, the thermal maturity of the sedimentary organic matter has some bearing on the likelihood of encountering hydrocarbon hazards during drilling operations (see Section II-A of Safety Manual). The purpose of this Appendix is to briefly summarize some of the measurements and interpretations which can be used to provide estimates of the thermal history of sedimentary organic matter.

The practical choice of methods to estimate the degree of thermochemical transformation depends on a number of factors, not the least of which is the availability of equipment and experienced personnel to make the measurement. Some of these methods are amenable to shipboard operation and in the future an effort may be made to obtain such data, especially at drilling sites critical from the standpoint of potential hydrocarbon hazards.

The commonly used measurements, their interrelationships and variation with degree of thermochemical transformation are summarized in Figure C-1, drawn from a number of sources.

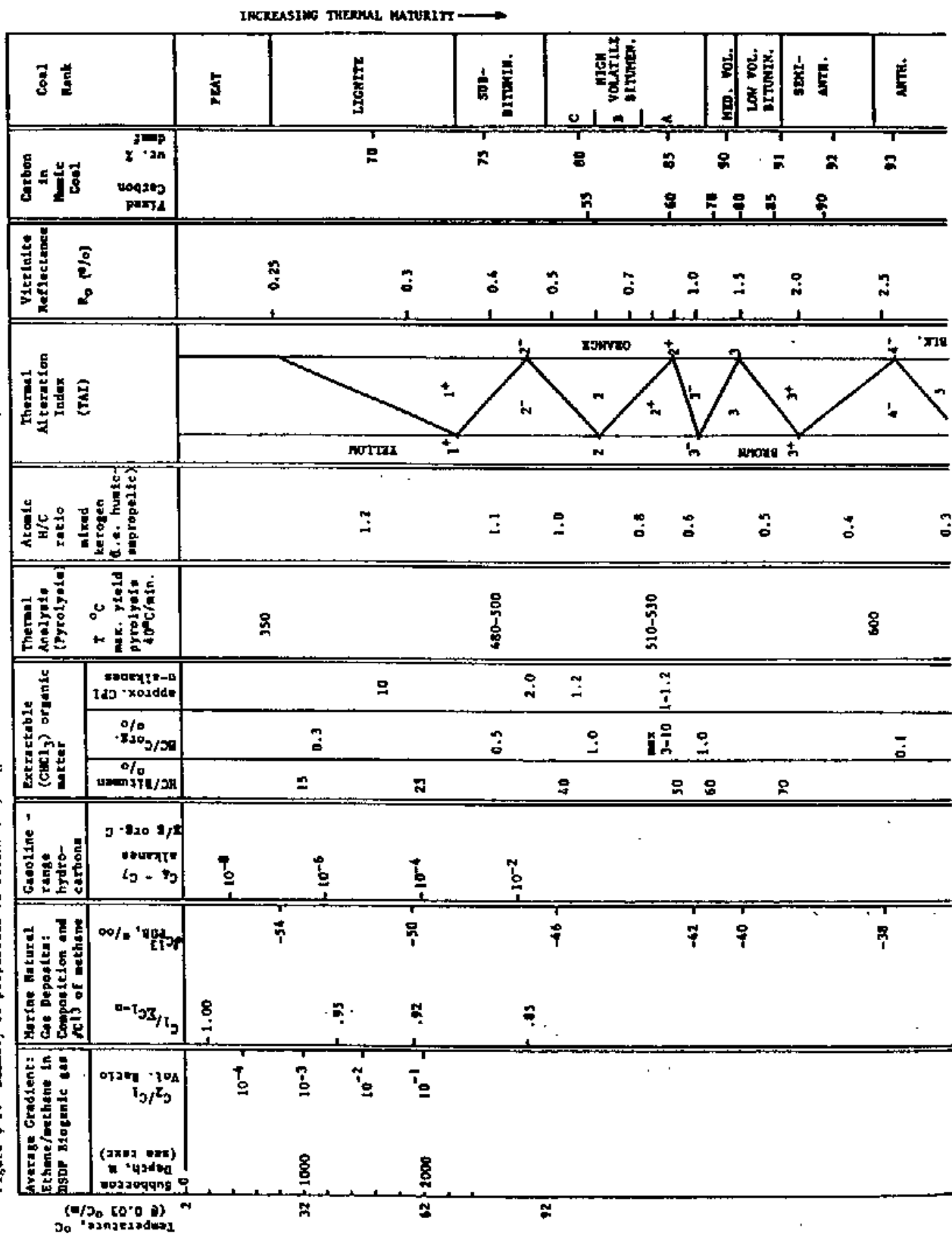
Except in the case of naturally occurring organic concentrates such as coal, native bitumen solids, and petroleum including natural gas, it is usually necessary to separate or concentrate the organic phase from the associated sediment prior to measurement of a property sensitive to thermal maturity. The relative difficulty with which this separation can be accomplished usually increases in the order gas<liquid<solid organic phases. However, the confidence and reliability of interpretations regarding thermal maturity are generally highest for measurements made on the solid organic phase. Accordingly, there is some trade-off between convenience of measurement and reliability of interpretation.

Some of the properties of sedimentary organic matter which are useful for the interpretation of thermal maturity are discussed below, in general order of the probable ease of shipboard implementation.

Chemical Composition of Sediment Gas

The hydrocarbon gases (C_1 - C_4) are the organic phase most readily separated from the sediment. If fresh wet sediment containing dissolved gas is allowed to equilibrate with a gas phase in a closed container at one atmosphere pressure and 25°C, the C_1 - C_4 gases will spontaneously and

Figure C-1. Summary of properties of sedimentary organic matter sensitive to temperature history.



almost completely partition into the gas phase. In deep sea sediments which contain typical amounts of biogenic methane dissolved in the pore water, this equilibration takes place when the core barrel is raised to the deck of the ship and gas pockets form within the corer. The methane provides the gas phase which effectively samples the level of C_2-C_4 hydrocarbons in the sediment. Samples of this type are routinely collected and analyzed on the GLOMAR CHALLENGER at the present time. An interpretation of DSDP gas pocket samples with respect to thermal maturity is summarized in column 1 of Figure C-1. Values of the C_2/C_1 volume ratio are shown, based on measurement of peak areas (peak height times peak width at half-height) corrected by attenuation factors and the C_2/C_1 response factor ratio of 1.1 for the appropriate concentration ranges of the constituents as measured by the Carle thermal conductivity detector. The C_2/C_1 ratios and the trend shown are average values for deep sea sediments containing biogenic methane. More specifically, the trend in C_2/C_1 ratio shown in column 1 of Figure C-1 refers to rapidly (150 m./m.y. sediment accumulation rate) and continuously deposited deep sea sediments, containing 0.2 to 0.5 percent organic carbon, with a normal (0.03°C/m) thermal gradient.

This interpretation, that the trend of increasing ethane (C_2) content with depth of burial in DSDP sediments reflects the thermal maturity of the organic matter in the sediments, is based on the observed variation of the C_2/C_1 ratio with the known or estimated age and temperature of the sediments from which the gas samples were collected. In nearly all cases where a series of samples were analyzed from over a significant depth interval (>100m), the C_2/C_1 trend was predictable from a knowledge of the sediment accumulation rate and the geothermal gradient. These data are reviewed in Section 2 of this appendix, (Review of Shipboard Gas Analyses, DSDP Legs 10-31). The simplest interpretation which is consistent with the observed variation of ethane content in DSDP gases is in situ generation of ethane (and heavier but generally undetectable hydrocarbons) by nonbiological chemical reactions at temperature-dependent rates. Alternative explanations to account for the presence of heavier hydrocarbons in DSDP gases such as upward diffusion/migration from depth and/or biochemical production of heavier hydrocarbons, would not be expected to be so consistently related to the age and temperature of the sediments in which the gases occur.

When present in deep sea sediments, dissolved biogenic methane provides a relatively constant background against which very slow thermochemical generation of hydrocarbons can be measured. In marine sediments, methane accumulates only in depositional environments where the sedimentation rate has been sufficiently rapid (>50m/m.y.) to preserve organic matter and cause complete removal of dissolved oxygen and sulfate from the pore water. Under these conditions biogenic methane production appears to be self-limiting and results in dissolved methane concentrations on the order of 10 mmole/l in the interstitial water. The amount of ethane (and heavier hydrocarbons) relative to the methane is variable over many

orders of magnitude (10^{-7} to 10^{-2}) and depends on (1) the amount of organic matter in the sediment from which hydrocarbons can be generated, and (2) the temperature history and the progress of thermochemical hydrocarbon-generating reactions. Except for unusual environments (e.g., the Cariaco Trench) the content of organic matter in methane-producing deep sea sediments is constant to within less than one order of magnitude (i.e., 0.1 to 0.5 wt. % organic carbon). Therefore temperature is the primary factor determining C_2 - C_5 hydrocarbon content of gases which are dominantly biogenic methane.

Carbon Isotopic Composition of Methane

The δC^{13} value of methane generally shows a consistent relation with the thermal maturity of the organic matter in the sediments which produce the gas. This general relation is summarized in column 2 of Figure C-1. There are two reasons for the observed relationship between the δC^{13} of methane and the thermal maturity of the organic matter or depth of burial. First, shallow methane is usually of biogenic origin and it is almost always isotopically light ($\delta C^{13} \sim -90$ to -60 ‰) while methane produced at depth by thermochemical decomposition of organic matter is usually heavier ($\delta C^{13} > -50$ ‰). Second, because of differences in the binding energies of isotopic molecules, the earliest formed detectable quantities of thermochemical methane will be isotopically light ($\delta C^{13} \sim -50$ ‰) while that formed later will be heavy ($\delta C^{13} \sim -30$ ‰). Biogenic methane generally does not escape from deep sea sediments, but remains dissolved in the buried interstitial waters. Consequently, there should be a region of overlap where the chemical and isotopic characteristics of biogenic methane become diluted and gradually obscured by methane and heavier hydrocarbons of thermochemical origin. This region should be at depths where temperatures of 60-90°C are achieved.

For the interpretation of the thermal maturity of the organic matter, the chemical composition of gas is usually less ambiguous and more easily obtained than the isotopic composition. However, methane gas with little or no accompanying ethane and higher hydrocarbons, is produced both at low and very high (incipient metamorphic) temperatures. If the geologic setting or some other evidence will not distinguish between these two types of dry gas occurrence, the δC^{13} of the methane should be unequivocal.

Gasoline-range Hydrocarbons

If fresh wet sediment is equilibrated in a closed container with a gas phase at one atmosphere pressure and boiling water temperature (100°C), then hydrocarbons in the range C_1 to C_7 will effectively partition into the gas phase. A sample of the gas phase can be withdrawn from the container, concentrated if necessary by injecting a large volume of the gas through a chilled sample loop, and analyzed by capillary column, flame ionization gas chromatography. This analysis could be done on board ship almost as readily as the permanent gas (C_1 - C_4) analysis, if the appropriate equipment were available.

Total C_4 - C_7 alkane hydrocarbons have been shown to be present in DSDP sediments at levels of 10^{-10} to 10^{-8} g per g of sediment, or 10^{-7} to 10^{-6} g per g of organic carbon. These same compounds are present at levels of about 10^{-2} g per g of organic carbon in sediments which have been subjected to temperatures sufficient to cause thermochemical production of petroleum hydrocarbons. This trend of increasing content of gasoline range hydrocarbons with increasing thermal maturity of the organic matter is summarized in column 3 of Figure C-1.

The normal (straight-chain) C_4 - C_7 isomers appear to be the compounds most commonly present at detectable levels in thermally immature sediments, while some of the iso (branched-chain) C_4 - C_7 alkanes such as 2,2-, 2,3-, 2,4-Dimethylpentanes and 3-Ethylpentane are more commonly undetectable.

Solvent-extractable Organic Matter

Wet sediment can be tested for oil-staining by washing with an organic solvent such as dichloromethane and examining the wash solution under ultraviolet light. Fluorescence suggests, but does not prove, the presence of a separate oil-wet organic phase such as migrated petroleum hydrocarbons.

The actual presence of indigenous or migrated heavy (C_{12} -plus) petroleum hydrocarbons must be confirmed by more detailed analyses. An oven-dried ($\sim 60^\circ\text{C}$) sample can be rapidly extracted with organic solvents using ultrasonic energy. The extract solution can be recovered by filtration or centrifugation and the concentration of extractable material quickly estimated by calibrated spectrofluorescence. In order to evaluate the possible significance of the extractable material in terms of thermal maturity or migrated hydrocarbons, it is necessary to obtain (1) an estimate of the amounts and relative proportions of hydrocarbons versus non-hydrocarbon (asphaltic) extractable materials, and (2) a gas chromatographic fingerprint of the saturated hydrocarbons. This can be accomplished by separating the extractable material on a silica-gel or alumina column wet-packed with a non-polar solvent. Before adding the extracted material to the top of the column, the more polar extraction solvent must first be removed from the extract solution by evaporation and displacement with a non-polar solvent which has a lower vapor pressure than the extraction solvent, such as heptane. The nominal saturated and aromatic (total) hydrocarbons can be eluted from the column with heptane and benzene, respectively, and their concentration estimated by quantitative gas chromatography.

Thermally immature sediment extracts usually contain only 10-25% hydrocarbons, while the extractable materials from mature or oil-stained sediments contain 50% or more hydrocarbons. In addition, the gas chromatographic "fingerprint" of the saturated hydrocarbons from mature sediments should resemble petroleum in having a smooth distribution of n-paraffins and a high proportion of resolved peaks relative to the hump of unresolved branched-cyclic material.

Thermal Analysis/Pyrolysis

A great deal can be determined about organic richness and thermal maturity of sediments from Thermal Analysis. Specialized equipment is required for controlled heating of the sediment in a stream of helium while monitoring the production of volatile organic compounds as a function of heating temperature. It is also possible to trap the volatile compounds liberated or produced from the rock by heating and to analyze them by gas chromatography.

When the sediment is heated at a constant rate of temperature increase (e.g., 40°C/min) volatile organic compounds are distilled from the sediment at low temperatures (30 to 350°C), and produced by thermal decomposition of the solid organic matter at higher temperatures (350 to 650°C). By integration of the detector response over the appropriate temperature intervals, it is possible to estimate the absolute amounts and relative proportions of liquid vs. solid organic matter. In addition, the temperature required to produce the maximum thermal decomposition of the solid organic matter is largely a function of the past temperature history experienced by the sediment. Organic matter in a sediment which has never been heated above 40-50°C, will begin to decompose thermally at about 350°C when heated at 40°C/min, while mature, petroleum-generating source rocks will not break down until temperatures of 520-550°C are reached.

In addition to the interpretations of organic richness and thermal maturity, the quality of the organic material produced by volatilization or thermal breakdown of the solid organic matter can be determined by trapping the products and analyzing them by gas chromatography.

The approximate temperature range of maximum pyrolysis yield is shown in column 5 for organic matter of different degrees of thermal maturity.

Chemical and Physical Properties of Solid Organic Matter Related to Maturity and Hydrocarbon Generation

The elemental chemical composition of coal and/or kerogen (atomic H/C, % C dry mineral matter free), the color of recognizable clastic organic particles (TAI), and the reflectance of vitrinite particles each change in a regular fashion with increasing degrees of thermal maturity, as shown in columns 6, 7, 8 and 9 of Figure C-1. The changes in these properties (and other properties such as BTU content) determine coal rank (column 10). The process of liquid hydrocarbon generation has been empirically and experimentally associated with the burial time and temperature combinations required to produce the high volatile bituminous rank of coal. Organic matter disseminated in sediments undergoes the same transition exhibited by the coal rank series in concentrated form. Therefore, if the disseminated organic matter is concentrated, and properties such as atomic H/C ratio, TAI or vitrinite reflectance determined, the diagenetic stage with respect to the process of hydrocarbon generation can be fairly accurately estimated. Concentrating the solid organic matter requires that the mineral matter

be dissolved with concentrated hydrofluoric and hydrochloric acids. This may not be a practical shipboard operation, thus it becomes important to establish the approximate correlations between measurements on solid organic matter and the characteristic changes in the gaseous and liquid organic phases, as shown in Figure C-1.

The generation of petroleum hydrocarbons from sedimentary organic matter is a necessary, but not a sufficient condition for the occurrence of petroleum. Therefore, from the standpoint of possible hydrocarbon hazards, the thermal maturity of the organic matter in the sediments being drilled is only one of the factors to be taken into consideration. It should not be concluded that it is safe to drill in sediments containing thermally immature organic matter without fear of hydrocarbon hazard. Conversely, it should not be concluded that it is unsafe to drill in sediments containing thermally mature organic matter. The temperature history and organic richness of sediments being penetrated is necessary background information, to be used along with a number of other geological and operational factors by shipboard personnel experienced in drilling operations to arrive at a judgement as to when the possible achievement of scientific objectives are outweighed by the possible hazards involved.

2. Review of Shipboard Gas Analyses, DSDP Legs 10-31

As a safety precaution, sediments cored in the Deep Sea Drilling Project are routinely examined for the presence of hydrocarbons. One procedure involves sampling gas expansion pockets in the cores. The gas samples are analyzed by gas chromatography on board the GLOMAR CHALLENGER; the balance of the gas and the unanalyzed samples are sent to shore-based laboratories for additional chemical and isotopic analyses. The sampling and analytical procedures have been described in Volume XIX, Initial Reports of the DSDP (Claypool, Presley and Kaplan, 1973). The gas analyses and δC^{13} measurements on gas samples from Legs 10, 11, 13, 14, 15, 18, 19, 23, 24, 27, 28, and 31 are summarized in tabular form, together with the locations, water depths, penetration depths, and physiographic names or descriptions. Copies of this table are available from the JOIDES Office on request.

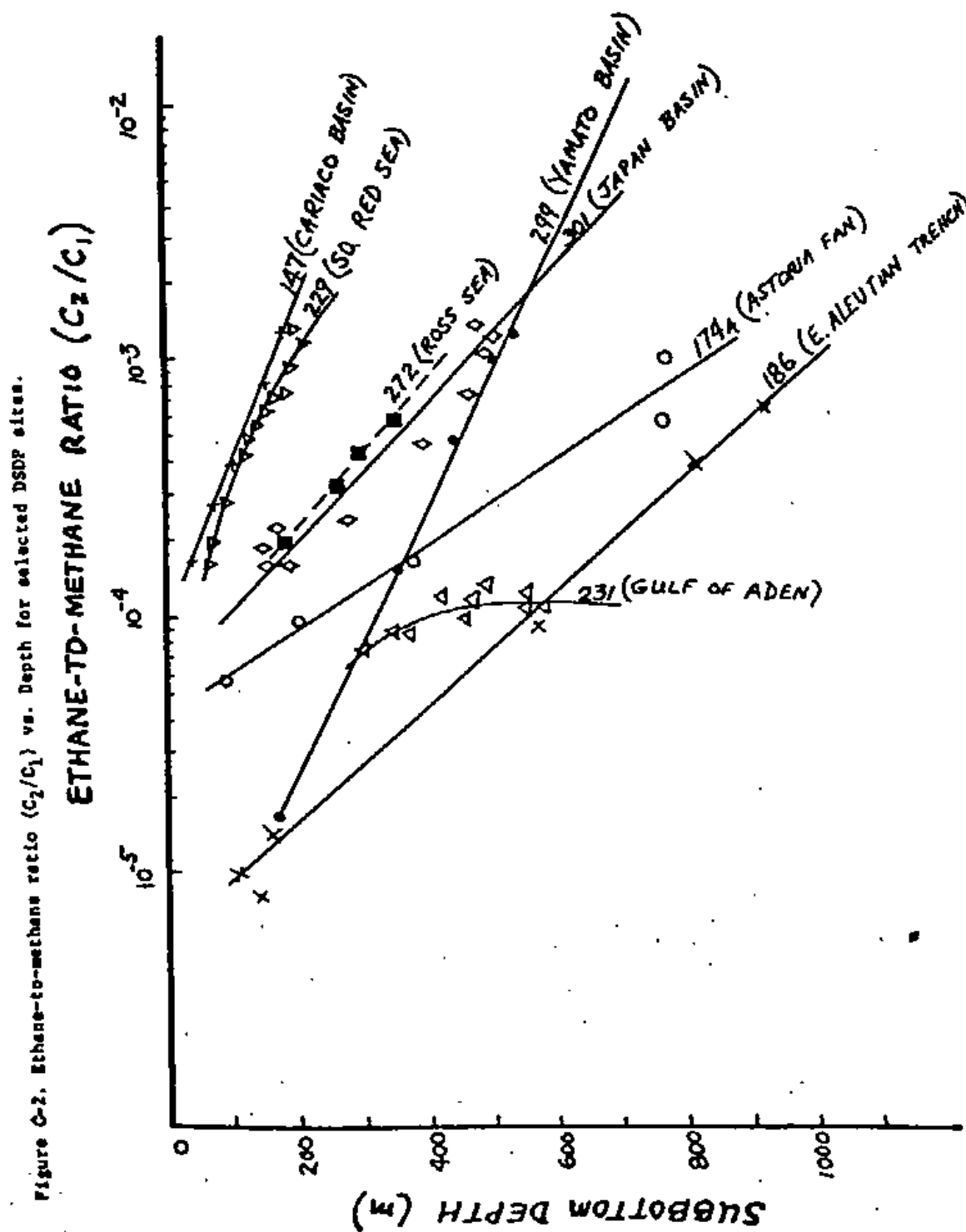
Results and Discussion

The chemical composition of DSDP sediment gases (expressed on an air-free basis) and the δC^{13} value of the methane in the gas samples have been established. Except for samples from one locality, the composition of the gas samples, with air gases excluded, consists of relatively pure methane with ethane contents ranging from undetectable to 0.1% by volume. Carbon dioxide is generally a significant component of the gas with typical contents on the order of 0.1 to 1%, but occasionally ranging as high as 15%. For the sites studied, except for samples from two localities, the δC^{13} values for methane range from -83 to -59 ‰ relative to the PDB marine carbonate standard. Both the chemical and isotopic characteristics are typical of biogenic methane in marine sediments.

As discussed elsewhere (Claypool and Kaplan, 1974), the δC^{13} of biogenic methane being produced at any instant is generally about 70‰ lighter than the CO_2 reservoir from which it is generated, due to a large kinetic isotope effect (Rosenfeld and Silverman, 1959). However, this instantaneous relationship is only apparent in the earliest stages of methane production in marine sediments, i.e., in the shallowest occurrences of methane in DSDP sediments. With increasing depth of burial, or during later stages of methane production within a given parcel of sediment, the δC^{13} of the cumulative methane produced generally becomes heavier as the dissolved CO_2 reservoir is increasingly depleted in C^{12} due to continued methane production. The ultimate δC^{13} value of the biogenic methane depends on all the other factors controlling the carbon isotopic composition of the dissolved CO_2 reservoir (i.e., rates of biogenic CO_2 production, carbonate dissolution, thermocatalytic decarboxylation, etc.) in addition to methane production. Generally, in sediments which have a significant calcareous component, the δC^{13} of the dissolved CO_2 is buffered at about 0 to +5‰ by dissolution of detrital carbonate. Under these conditions coexisting biogenic methane has δC^{13} values in the range -85 to -55‰. However, the carbon isotopic composition of the dissolved CO_2 reservoir, in organic-rich noncalcareous sediments (diatomites, peats) can be driven to extremely heavy δC^{13} values (+20 to +25‰) and this can result in the production of unusually heavy biogenic methane (-50 to -45‰).

The CO_2 content of the gas samples is strictly a function of the pH and the concentration of total dissolved carbonate species in the pore water. High CO_2 content in the gas is generally mirrored by high carbonate alkalinity, where a direct comparison is possible (e.g. Hole 147, Leg 15; see Hammond and others, 1973, Fig. 1, and Hammond 1973, Fig. 13 in Initial Reports, v. XX). However, there are notable exceptions where high carbonate alkalinities are not reflected in high CO_2 contents in the gases. In these cases the pore water system must be maintained at high pH values, possibly due to rapid methane generation with slow or negligible biogenic CO_2 production.

The ethane content of DSDP gas samples is summarized for selected holes in Fig. C-2, where ethane-to-methane ratio (C_2/C_1) is shown as a function of depth of burial on a semi-log plot. In most cases, where gas samples have been recovered from throughout the section penetrated, the C_2/C_1 ratio increases exponentially with increasing depth of burial. Moreover, both the relative amount of ethane in the gas and the rate of increase in the C_2/C_1 ratio are proportional to temperature. For example, the coldest sediments, in terms of both bottom water temperature and thermal gradient, are probably in Hole 186 from the Eastern Aleutian Trench. Gas samples from this hole are lowest in ethane content for any given depth of burial, among the samples plotted in Fig. C-2. In contrast, Hole 229 in the South Red Sea has a bottom water temperature of 22°C and a measured thermal gradient of 0.07°C/m. The gas samples from this hole have high ethane contents at very shallow depths, and the relative ethane content increases very rapidly over the next 150 m. The



section at Hole 186 is Pleistocene to early Pliocene (1 m.y.) in age, while sediments at Hole 229 were deposited in the last 350,000 years.

Gas samples from other DSDP holes which are plotted in Fig. C-2 are believed to represent intermediate temperature situations. Two notable exceptions in Fig. C-2 are Hole 272 from the Ross Sea and Hole 147 from the Cariaco basin. These cases are believed to illustrate the effects of age and organic richness, respectively. The gas samples from Hole 272 were obtained from sediments of Middle to Early Miocene age beneath an unconformity, and are thus several times older than the other sedimentary sections represented in Fig. C-2. Even though the present-day temperatures in Hole 272 may be relatively cold, the sediments may have been more deeply buried, and therefore warmer, in the past; moreover, the greater age of these sediments would permit the ethane generating chemical reactions, which are presumably the in situ spontaneous decomposition of detrital organic precursors, to be further advanced at any given temperature.

At Hole 147 the bottom water temperatures are relatively warm (17°C) but there is no reason to expect that the thermal gradient is unusually high. However, the level of organic carbon in the sediments of Hole 147 is much higher than at other localities shown on Fig. C-2 (2 to 4% vs. .1 to 1%). An increased content of ethane precursors may explain why the ethane generation process is apparently more effective in the Cariaco basin at somewhat lower temperatures than in the southern Red Sea.

Gas of anomalous composition was encountered at two DSDP drilling sites. At site 176, on the continental shelf off the coast of Oregon, methane gas with δC_{13} values in the range -59 to -47‰ occurred at very shallow depths (23 to 39 m subbottom). The carbon isotopic composition of the methane in these samples approaches that of methane associated with petroleum, however ethane and higher hydrocarbons were below the limit of detection. This gas is most likely not associated with petroleum, but is a mixture of residual biogenic methane which has undergone partial bacterial oxidation during a Pleistocene regression of sea level, and newly formed methane which was generated with the return of anoxic conditions. Evidence for bacterial oxidation of methane is present in these sediments in the form of unusual diagenetic carbonate concretions which have δC_{13} values (-35‰) that could only be due to oxidized methane.

The other locality with gas of anomalous composition by DSDP standards is site 88, drilled above a presumed salt dome in the Campeche-Sigsbee province of the Gulf of Mexico. The gas from this hole, at depths of 102 to 135 m is chemically and isotopically identical to natural gas associated with petroleum. This undoubtedly represents a case where DSDP operations penetrated a petroleum accumulation. The gas is presently in sediments of Pleistocene age but most probably originated at much greater depths, moved up (with the salt?) and was emplaced at shallow burial depths during a Pleistocene low stand of sea level. At the present water depth of this locality (2532 m) the gas should be frozen in place as the solid clathrate hydrate, which may

have prevented escape of the gas from the subsurface. Drilling was terminated at this site before the scientific objective (penetration of the salt) was achieved. There is at least a fair chance that liquid petroleum would have been encountered at this site with further drilling. Whether, if present, it would have been an "oil show" similar to that of the DSDP Leg 1 Challenger Knoll, or an occurrence of larger magnitude is, fortunately, still unknown.

Summary: The Significance of Gas Occurrence in Deep Sea Sediments

Obvious shows of gas have been encountered in at least 40 of the 220 holes drilled through Leg 31 of the Deep Sea Drilling Project. In all cases except one (Hole 88, Leg 10) the gas sampled and analyzed has been relatively pure methane of apparent bacterial origin (marsh gas). The carbon isotopic composition of methane in DSDP gas samples is related to the amount and isotopic composition of coexisting bicarbonate in the pore water. The nature of this relationship indicates that the methane originates primarily from respiration (CO_2 reduction) by anaerobic bacteria in the sediment. The process is exactly analogous to, and occurs just after or below the process of bacterial sulfate reduction.

The quantity of methane generated by this process in deep sea sediments has never been directly determined, but has been indirectly estimated to be on the order of 10 to 20 mmol per liter of interstitial water. This concentration of gas is insufficient to saturate buried sea water at pressures and temperatures corresponding to burial depths of 1 km or less in sediments overlain by water depths of 0.5 km or more, so that a free gas phase should not be present in the subsurface, but as methane dissolved in the interstitial water of the sediments. Under these conditions, there is little tendency for the gas to migrate and accumulate, therefore these gas deposits have only minimal economic significance. Conditions which would favor the formation of a free gas phase, i.e. reduction of pressure by lowering of sea level or uplift and erosion of marine sediments, could lead to the formation of significant gas deposits of biogenic origin.

The principle significance of these gas deposits is their value as indicators of degrees of organic metamorphism. The exsolution of biogenic methane from the sediments as they are brought up from beneath the sea floor to the deck of the drilling vessel provides a gas phase which representatively samples indigenous hydrocarbons of thermocatalytic origin. Ethane and higher hydrocarbons will partition into the gas phase in amounts which depend on: 1) the total concentration of the hydrocarbons in the sediment; 2) the vapor pressures of the individual hydrocarbons; 3) temperature and pressure. With the sampling and analytical procedures employed in the Deep Sea Drilling Project to date, ethane is the only hydrocarbon other than methane routinely detected. Propane, butanes, etc. are also present in many cases but in amounts less than the level of detection by the thermal conductivity detector of the gas chromatograph.

3. Mud Expansion as an Index of Methane Concentration in Deep Sea Sediments

The potential hazards of drilling in gas-charged sediments along with recommended precautions and some qualitative characteristics bearing on the origin of the gas have been discussed in previous sections of this Safety Manual. As emphasized earlier, it is not the origin or composition of the gas, but the total quantity and the possibility of trapping and accumulation which pose the potential danger.

Gas shows are to be expected when drilling in sediment which has accumulated at rates in excess of 50 meters per million years. Therefore it may become important to attempt to distinguish between the expected background amounts of gas in the sediment, and gas concentrations which might pose a hazard. It is impossible to set rigid quantitative guidelines which would be applicable under all circumstances. However a useful rule-of-thumb for evaluation of the significance of gas shows may be the apparent degree of saturation of the interstitial water with methane.

If the porosity and the subsurface temperature and pressure of the sediment can be estimated or measured, then it is possible to calculate the standard volume of gas which could be dissolved in the pore water of a given volume of sediment under burial conditions.

The approximate solubility of methane in water as a function of pressure and temperature at seawater salinity is given in Table C-2. The theoretical degree of expansion due to exsolution of methane at saturation from the pore water can be estimated from the ratio

$$\frac{\text{volume of gas}}{\text{volume of wet sediment}} \quad (1)$$

which is obtained by multiplying the porosity (as a fraction) times the appropriate methane solubility from Table C-2. This should be compared with the measured degree of expansion of the sediment which will be available if the pressure core-barrel is used as the ratio

$$\frac{\text{volume of gas bled off}}{\text{volume of pressure core-barrel}} \quad (2)$$

If the pressure core-barrel is not available, a minimum estimate of the ratio for comparison would be

$$\frac{\text{length of gas expansion pockets in core liner}}{\text{total length of core liner}} \quad (3)$$

When the estimate of gas content given by ratios (2) or (3) begins to approach the value of theoretical pore water saturation under in situ conditions, as given by ratio (1), the likelihood of encountering a free gas phase in the subsurface would be increased (if gas hydrates were not stable). A free gas phase has a greatly increased capacity to store pressure in the subsurface, compared to liquids which are largely incompressible.

Two important points to be kept in mind are (i) that under the proper P-T conditions interstitial water can contain up to approximately 200 times its volume in methane (at standard conditions) as the solid methane hydrate, without the formation of a free gas phase; and (ii) that the sediment plugs in the core liner are not a perfect seal for the escape of gas, so that ratio (3) is always a minimum estimate of gas content.

Table C-2 Methane solubility in water as a function of temperature and pressure at seawater salinity, ml (STP) CH₄/ml H₂O.

	Temperature (°C)									
	5	10	15	20	25	30	35	40	45	50
50	*	1.44	1.34	1.23	1.18	1.14	1.08	1.03	0.96	0.88
100	*	*	2.16	1.95	1.87	1.79	1.71	1.62	1.54	1.49
150	*	*	*	2.73	2.52	2.40	2.26	2.15	2.06	1.97
200	*	*	*	3.15	2.96	2.80	2.62	2.50	2.37	2.28
250	*	*	*	*	3.30	3.14	2.98	2.83	2.71	2.63
300	*	*	*	*	3.60	3.40	3.29	3.21	2.95	2.98
350	*	*	*	*	3.91	3.76	3.60	3.50	3.40	3.27
400	*	*	*	*	4.12	4.00	3.86	3.80	3.69	3.58
450	*	*	*	*	*	4.24	4.10	4.00	3.89	3.79
500	*	*	*	*	*	4.44	4.33	4.20	4.06	4.01
550	*	*	*	*	*	4.60	4.46	4.38	4.24	4.14
600	*	*	*	*	*	4.82	4.71	4.60	4.48	4.36
650	*	*	*	*	*	4.97	4.85	4.72	4.62	4.50
700	*	*	*	*	*	5.07	4.93	4.82	4.72	4.63

* Methane hydrate stable under these conditions; equilibrium solubility has not been accurately measured but appears to be about 30% of the extrapolated solubility; however, about 200 ml of methane can theoretically be contained per ml water without the formation of a free gas phase.

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