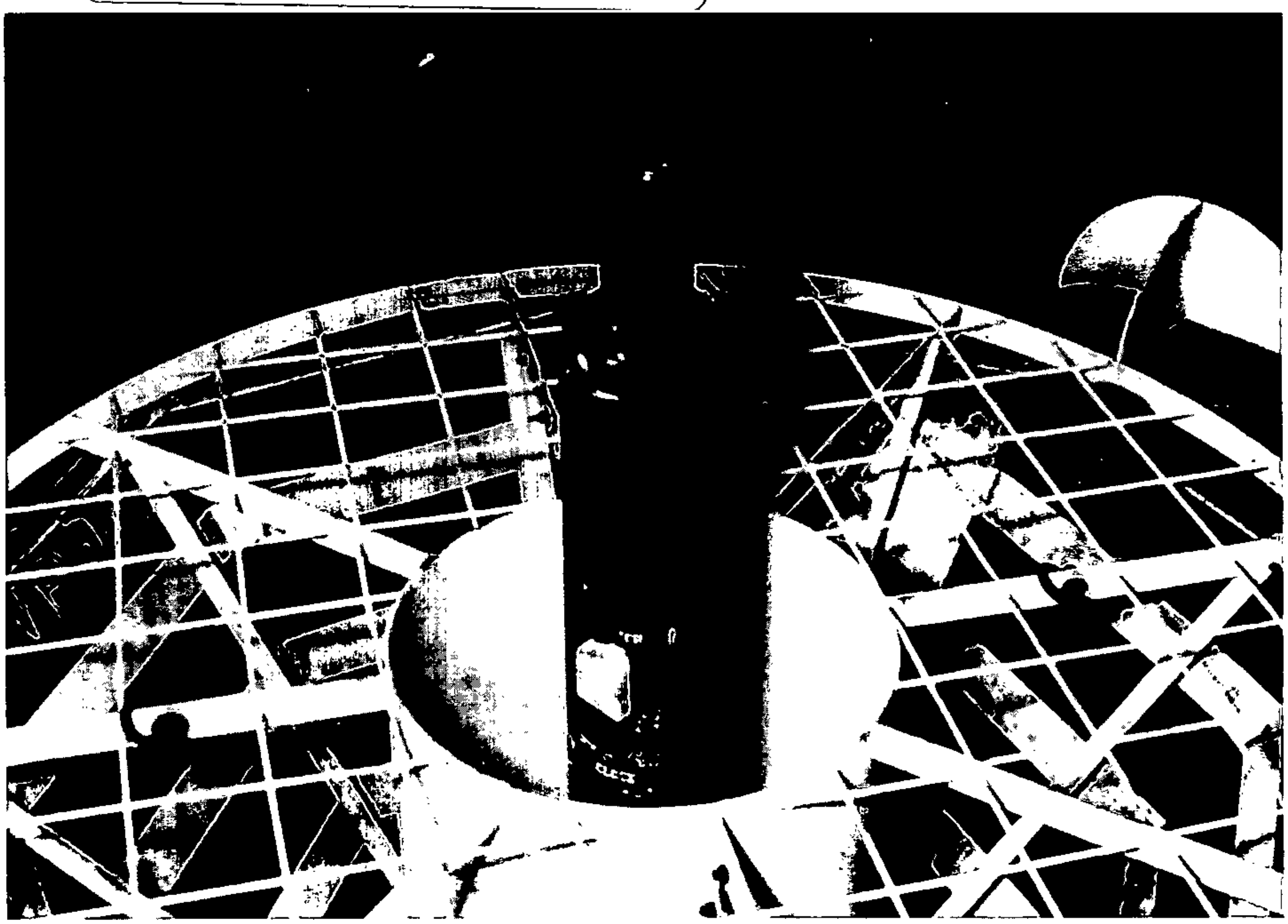
Joint Oceanographic Institutions for Deep Earth Sampling

JOIDES Journal

Ocean Drilling Program Guidelines for Pollution Prevention and Safety

Volume 18, Special Issue No. 7, October 1992



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Preface

All drilling operations involve some risk of accident or pollution. This has been recognized throughout the history of the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP). Policies to minimize drilling hazards originally developed during DSDP have been continually updated and implemented for ODP.

This special issue of the *JOIDES Journal* is devoted to a new edition of the Guidelines for Pollution Prevention and Safety of ODP. These guidelines were developed by the JOIDES Pollution Prevention and Safety Panel (PPSP). PPSP is composed of petroleum geologists, geophysicists, engineers and organic geochemists drawn from industry, government and academia, who are recognized authorities in the fields of marine research and offshore oil exploration. They provide independent advice to ODP.

Introduction

The value of the scientific objectives that are sought in ODP must be balanced against potential hazards so that ODP will achieve these objectives without falling below acceptable standards of safety and pollution prevention. With diligent planning and careful operational procedures, it is possible to minimize risks and achieve desired goals.

Adherence to the old adage of "An ounce of prevention is worth a pound of cure" offers the surest route to safety and prevention of pollution. Money and time spent on extra care in preliminary site surveys, choice of site locations, and in planning drilling operations may forestall an accident that could cause loss of life, property and damage to the environment, and could also cause termination of this major international scientific endeavor.

The diverse sites planned for ODP drilling involve additional hazards not encountered in previous DSDP drilling. Holes are now planned for deeper sediment penetration, in shallower water on continental margin sites. Moreover, *JOIDES Resolution (Sedco/BP 471)* continues to operate in a riserless mode. It follows that ODP must continue to face drilling hazards inherent in operating without a drilling riser to the surface, with lack of return circulation, and without standard blowout preventors. Although improved seismic surveys, an expanded borehole logging program and advanced hydrocarbon monitoring capabilities will provide additional information for decisions on safety and pollution matters, it is evident that emphasis on pollution prevention and safety must increase with time.

Principal Hazards

A. Oil and Gas Escape and Blowouts

The main hazard in scientific ocean drilling, with respect to pollution prevention and safety, is the possibility of encountering a charged reservoir, allowing oil or hydrocarbon gas to escape in large quantities into the sea and atmosphere. Because natural submarine seeps of both oil and gas exist in many parts of the world, apparently with little deleterious effect on the environment, it is difficult to say what amounts of oil or gas released into the sea or atmosphere by drilling operations should be termed hazardous. Certainly, as a pollutant, oil must be considered more serious than gas. On the other hand, as a hazard to personnel and property, gas is more dangerous than oil because of its mobility, high flammability, negative effect on water buoyancy, and difficulties in controlling its pressure.

1) Hydrocarbon origin and occurrences

The term "petroleum" is applicable to any hydrocarbon substance, although it is popularly reserved for crude oil, natural gas and asphalt. Mixtures of petroleum hydrocarbons exist as gaseous, liquid and solid phases depending on temperature, pressure and composition of the system. Under earth surface conditions, C_1-C_4 hydrocarbons (methane, ethane, propane and butane) are predominantly in the gaseous phase, while C_5 and heavier hydrocarbons are predominantly liquid.

Hydrocarbon gases, largely methane (C_1), may be generated in significant quantities from organic matter in sediments, either under near-surface conditions by bacterial action (Claypool, 1974) or at greater depths by thermochemical action (Schoell, 1988). 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 reach 50° to 150° C (typically at burial depths of 1,500-5,000 m for average geothermal gradients). Hydrocarbon gases are generated with the oil, and although they consist largely of methane, they usually include quantities of ethane (C_2), propane (C_3), butane (C_4) and heavier hydrocarbons. Thermochemical conversion of organic matter to hydrocarbons continues at accelerating rates with increasing depth and temperature, until all organic matter including the oil itself has been converted largely to methane and carbon-rich residues.

The apparent relationship of gas and liquid hydrocarbons with different modes of genesis to depth and temperature is shown in Figure 1. It should be stressed that although biogenic hydrocarbons are generated at relatively shallow depths and thermochemical hydrocarbons at relatively greater depths, either may be found at any drilling depth because of migration, 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 that contain sufficient contents of organic matter. Biogenic methane can usually be distinguished from thermochemical methane by means of isotopic ratio mass spectrometry; the biogenic form has a distinctly greater abundance of light carbon isotope ^{12}C relative to the heavy carbon isotope ^{13}C. Although thermochemical methane is formed along with ethane and heavier hydrocarbons in the

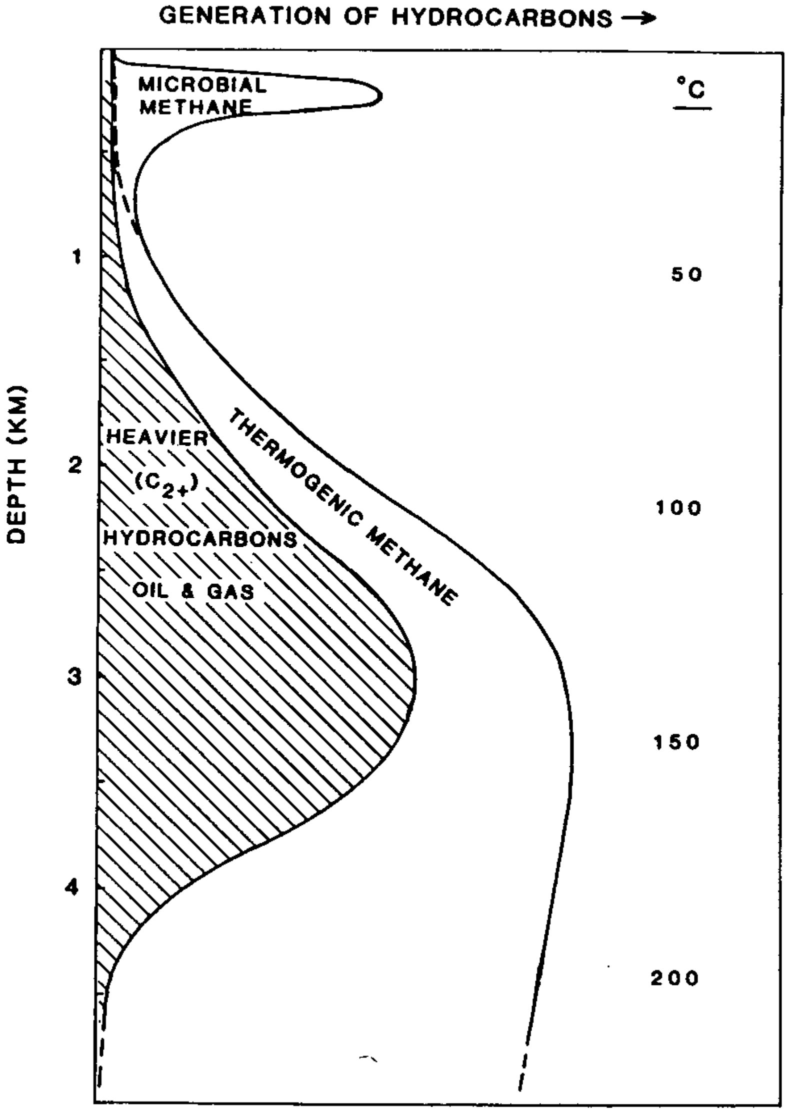


Figure 1. Relation of generation of methane and heavier hydrocarbons to depth of burial and temperature, and the relation between the genesis of microbial methane and thermogenic methane. (After Hedberg, H.,1974, *Amer. Assoc. Petrol. Geol. Bull.*, 58, 661-673).

early stages of hydrocarbon generation, the ratio of methane to ethane gradually decreases as hydrocarbons of thermochemical origin become more abundant.

More complete discussion of geologic factors involved in the origin and occurrence of petroleum is given in the following references:

Tissot, B.P. and Welte, D.H., 1984, *Petroleum Formation and Occurrence* (2nd Ed.), Berlin: Springer-Verlag, 538p.

Hunt, J.M., 1979, *Petroleum geochemistry and geology*: San Francisco, W.H. Freeman and Co., 618 p.

Both biogenic and thermochemical methane may be found in many ODP boreholes. There is no appreciable difference in their physical and chemical properties. Both can catch fire and cause blowouts. Both can be associated with some ethane and can occur in substantial quantities at very shallow depths. The only significant difference is that the conditions that produce thermochemical methane may also produce liquid oil, while oil of microbial origin is unknown.

A common misconception is that if methane is identified as biogenic, it can be disregarded as a safety hazard. A serious blowout occurred in offshore drilling in Cook Inlet, Alaska, apparently due to biogenic gas. Also, one of the world's largest gas fields and more than 20% of the world's gas reserves are apparently biogenic. It has been wrongly suggested that if methane/ethane or $^{12}C/^{13}C$ ratios exceed a certain value, gas dangers can be dismissed because it is only "marsh gas", not true thermogenic gas. *It is the quantity of gas present in reservoir strata rather than its origin that is of primary concern.*

The JOIDES Pollution Prevention and Safety Panel (usually referred to as the Safety Panel or PPSP) is strongly in favor of getting all information possible on the character of hydrocarbons in ocean sediments. However, PPSP deplores as a menace, rather than an aid to safety, the setting of "magic numbers" as substitutes for balanced judgment based on the multitude of geological, geochemical, operational and experience factors that should enter into decision-making concerning safety. *Arbitrarily imposed numerical guidelines for safety decisions are dangerous, because numerical guidelines may tend to be used blindly as crutches to obscure sound and reasoned judgment.*

2) Causes and dangers of blowouts

In oil well-drilling operations, formation fluids (water, oil or gas) will flow into the well bore when the pressure of the fluid in the reservoir exceeds the pressure in the drill hole. If the fluid entering the well bore is less dense than the drilling fluid, it will move upward in response to buoyancy.

When the formation fluid is gas, gas-charged water or gas-charged oil, it may permeate the drilling fluid, causing it to be filled with gas bubbles ("gas-cut"), thus diminishing the drilling fluid's density and ability to exert pressure on surrounding formations. Gas entering the well bore undergoes rapid expansion due to pressure reduction while traveling up the hole. Because of the confinement of the narrow borehole, increasing expansion of gas in the drilling fluid as it moves upward causes a flow of displaced drilling fluid from the hole mouth, further reducing the weight and pressure of the fluid column in the hole. The consequence is a "chain reaction." Gas enters the hole at ever-increasing rates as the pressure differential between gas-bearing formation and hole is increased. If not promptly brought under control, the process results in violent ejection of drilling fluid, which results in a "wild", unrestrained flow of gas or gas-charged formation fluid at the surface. Such an event is called a "blowout" and is extremely dangerous to life, property and the environment.

3) Differences in blowout risks between ODP and oil drilling operations

Elaborate measures are employed by the petroleum industry to prevent blowout occurrences: weighting of drilling muds, application of back pressure with pumps, use of mechanical blowout preventors, etc. In ODP operations, conditions are very different from customary oil and gas drilling, mainly due to lack of means for return circulation, use of sea water as a drilling fluid rather than heavy drilling mud, lack of a riser, and generally greater water depths involved. In ODP operations, gas encountered under pressure sufficient to cause it to enter the hole, permeate the sea water drilling fluid, and move upward would be confined only until it reached the ocean floor or the base of soupy, fluid sediment that often immediately underlies the sea floor. Above this point, gas continuing upward would tend to dissipate away from the borehole top into sea water and would reach the ocean surface in lower, perhaps imperceptible, concentrations over a broad area, with dimensions proportionate to the water depth the gas traversed.

Considering the great water depths usually involved in ODP drilling, there is relatively less danger of violent discharge of gas at the sea surface. However, means of controlling gas flow into the hole in ODP operations are limited. Moreover, even though the escape of gas or oil at the ocean surface from holes drilled in water depths of thousands of meters might be so diffuse as not to be readily discernible, total pollution of the ocean by hydrocarbons might be even greater than in a violent blowout.

A gas blowout imperils the vessel and crew in several ways: releasing toxic gases, triggering fires, and causing a loss of buoyancy due to charging surrounding sea-water with gas bubbles. The shallower the water at the drill site, the greater the potential of danger of buoyancy loss. Hydrogen sulfide (H_2S) is the principal noxious gas that might be released. H_2S is easily detected using commercially available monitors and is identifiable (but only in low concentrations) by its characteristic odor of rotten eggs.

The greatest fire danger on *JOIDES Resolution* would result if a blowout occurred *through* the drill pipe. In relatively shallow water, gas escaping to the surface from around the drill pipe may present a fire hazard. ODP drill crews are trained in standard oil field practices to avoid and control these possibilities. Buoyancy impairment is unlikely in water depths usually encountered at ODP sites. However, buoyancy problems have occurred at least twice in commercial drilling for oil in shallow waters and cannot be ignored at shallow ODP sites.

B. Inter-communication between Reservoirs and Exchange of Fluids

Situations can occur where formation fluids from deep, overpressured zones, flowing up the borehole, encounter shallower, lower-pressured zones. Under these conditions, the higher pressured fluids (oil, gas or water) may enter a zone that opens to the sea floor via fractures or permeable beds, resulting in an uncontrollable leak. The higher pressured fluids may charge shallower zones with fluids having more than normal hydrostatic pressures, thus making even shallow future drilling in the area hazardous. It is also possible, though not likely under most ODP conditions, that deep, saline formation water might contaminate shallower, fresh water aquifers in this way.

C. Drilling Active Ridges

High temperature hydrothermal systems close to magma chambers present special hazards for scientific ocean drilling. Behavior of water in hydrothermal systems is governed by pressure-volume-temperature (PVT) relationships. On the accompanying graph (Figure 2), specific volume (V) of water at constant T is plotted as a function of P. Below the critical T of water (374°C), there is an abrupt change of slope corresponding to the phase change resulting from boiling. Above the critical T, rate of change of V with P is gradual. With regard to drilling hazards, it is important to avoid drilling into rocks where P and T conditions indicate that a rapid increase in V of water would occur with increase in T or decrease in P. For example, drilling into a 360°C hydrothermal system at a P of 200 bars (about 2,000 m total sub-sea depth) would be unsafe, because a small movement of water up the drill pipe could cause water to flash to steam. In summary, the upper limit of T that is safe to drill depends on P at that T. For a given total sub-sea depth, it is necessary to set a maximum T to which drilling may be attempted. This requirement emphasizes the need to know bottom hole temperatures in order to ensure safe drilling conditions.

Geochemical considerations, together with past drilling experience and direct observations and sampling from research submersibles, have shown that excessive H_2S may interplay with high temperature to complicate active ridge drilling further. H_2S is a transparent, colorless, flammable, heavier-than-air gas that is lethal in concentrations measured in a few hundred ppm. Below 100 ppm, this gas is characterized by its "rotten egg" odor. However, over a period of a few minutes in the higher range of this concentration limit, ability to smell this gas is lost. H_2S solubility in water is a function of PVT conditions. This fact dictates a safety approach in which depths and T anticipated at specific drill sites determine safety measures to be taken for a given active ridge drilling leg. This approach was followed in drilling on the Juan de Fuca Ridge and Escanaba Trough (Leg 139). Extensive safety procedures for avoiding H_2S-related accidents have been spelled out for Leg 139 in the following publication:

Howard, S.P., and Reudelhuber, D.H., 1991, Hydrogen Sulfide-High Temperature Drilling Contingency Plan, Ocean Drilling Program, Leg 139 Sedimentary Ridge Scientific Drilling Operations; Rig Contractor - Underseas Drilling, Inc.; Drill Ship - Sedco/BP471 (6/13/91-Rev. 7); Ocean Drilling Program, *Texas A&M University Technical Note 16*, p. 1-53.

D. Other Hazards

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

While not detailed here, it is mandatory that all safety measures used in oil field operations and on drilling vessels, such as wearing safety hats, observing no smoking areas, and following emergency blowout and fire procedures, be adhered to. It is also essential that measures be taken to prevent pollution of the environment by any of the operations incidental to ODP.

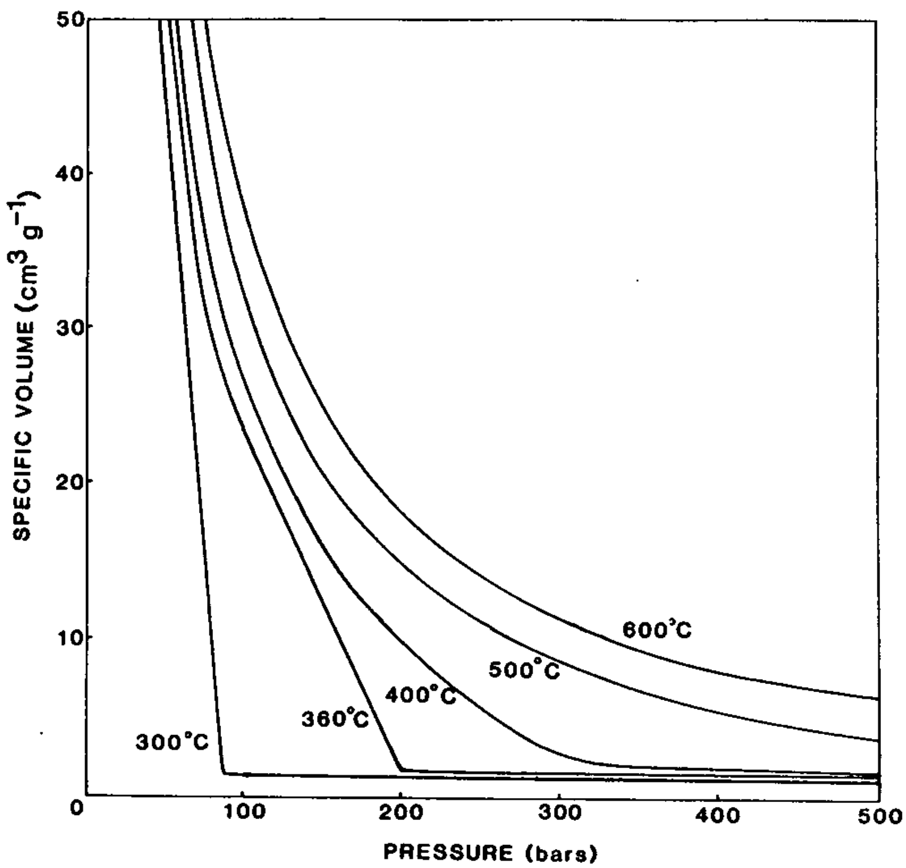


Figure 2. Specific volume of water at constant temperature as a function of pressure. (After Kennedy and Holser, 1966.)

General Observations of Precautionary Measures, Responsibilities, Information Requirements and PPSP Procedures

Subjects considered most important by PPSP are treated below under five topics:

1) choice of reasonably safe drill sites;
2) proper planning for the drilling program at each site;
3) early detection and anticipation of hydrocarbons and high fluid pressures;
4) measures for coping with fluid flows; and
5) measures for hole abandonment.

Care in the first of these, choice of reasonably safe sites, probably offers the greatest insurance against trouble.

It is the responsibility of those who plan each ODP leg to consider the above topics in both advanced planning and in the course of shipboard operations. It is also their responsibility to propose drill sites and programs they can support as being reasonably safe. The function of PPSP is to review proposals of sites and drilling programs as a backup to insure safety.

Those who plan drilling legs should do so only after thoroughly considering possible hazards and precautions outlined in these guidelines and adjusting their proposals accordingly. The attitude that the planners' involvement is only with science and that safety is exclusively the concern of PPSP is incorrect. Decisions on risks should be made with the recognition that the result of an accident or polluting incident will not be limited to a single hole or leg, but could affect the safety of the ship and crew and jeopardize the future of ODP.

Co-Chief Scientists of each leg are responsible for presenting sufficient data to PPSP to allow thorough evaluation of the above listed safety components for each drill site. Unless adequate data are provided, PPSP will refuse a proposed site. Moreover, the review data must be provided in time to allow study by PPSP members in advance of the formal review meeting. Advice on the conduct of the Safety Review Meeting is given in Appendix 1. Only definitely identified locations can be approved. If a location is subsequently moved, it cannot be considered to have been approved by PPSP.

Once drilling operations have commenced, responsibility for safety and pollution measures, including cessation of drilling, lies with the Science Operator's Shipboard Operations Superintendent. The Operations Superintendent relies on shipboard scientific and technical staff for prompt hydrocarbon analysis of all cores. Co-Chief Scientists are responsible for hydrocarbon monitoring; they are in charge of the scientific staff and laboratories. Co-Chief Scientists must not allow operations to continue at any time they feel that the safety guidelines detailed here are not being met. Advice on hydrocarbon monitoring is given in Appendix 2.

The Operations Superintendent and both Co-Chief Scientists should be present at the Safety Review Meeting for their drilling leg. On any leg where the geology of the region is favorable for petroleum occurrence, the shipboard scientific staff should include a hydrocarbon chemist and petroleum geologist with significant experience in planning and evaluating exploration and development wells drilled for oil and gas.

Precautions in Choice of Drill Sites

A. Thickness and Character of Underlying Sedimentary Strata

It is basic to pollution prevention and safety to make the best possible estimate of thickness of the sedimentary section at drill sites and to infer the nature of rocks to be penetrated. Knowledge of thickness of sedimentary rock above igneous or metamorphic basement is most useful in deciding whether a drill site has potential petroleum hazards resulting from thermochemical action on organic matter in the sediments. It is difficult to predict whether there has been an adequate supply of organic matter in the section to have allowed substantial petroleum generation. However, seismic data usually provide adequate information on sedimentary rock thickness at a proposed drill site. If there is no definite information on the absence of petroleum source material, thick sedimentary sections (1500m or more) must always be considered possible progenitors of petroleum and should be drilled with appropriate caution.

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

Sediment sections less than 1000m thick usually have not experienced sufficient heating to generate abundant petroleum. Areas of thin sediments are therefore relatively free of petroleum hazards, provided the following conditions are also fulfilled:

1) these areas have no possibility of having once been more deeply buried;
2) such areas are not pinch-out margins of thicker downslope sedimentary sections from which lateral migration of hydrocarbons could have taken place; and
3) such areas cannot have experienced greater than normal heat flow.

In general, PPSP considers central oceanic areas, with 500m or less of sediment above basement, to be nearly free of petroleum hazards. Even in such areas, however, consideration must be given to the possibility that older sedimentary sections may underlie acoustic basement or that biogenic methane may be present.

Obviously, hydrocarbon hazards are enhanced if good potential reservoir strata are present in the section. This factor has an important modifying effect on safety conclusions based on sedimentary thicknesses and organic contents. Seismic data and regional geologic considerations may give helpful information on probability of presence of substantial reservoirs.

Anticipated presence of evaporites, overpressured shales, gas-hydrate zones, and other seals, below which hydrocarbons may be trapped, also has an important bearing on the depth to which a drill hole can be safely carried. Presence of diapirs is a danger signal.

B. Structural Attitude and Probability of Traps

At least one continuous seismic profile must be obtained across any prospective drilling site, and two profiles intersecting at approximately right angles must cross at prospective sites on shelves, slopes and rises, or at any site where a single profile suggests the possibility of a trap. Features of significance on seismic profiles include anticlines, faults, pinchouts, unconformities, etc. Any sort of structural or stratigraphic trap should be avoided in choice of drilling locations. While reliance must be primarily on seismic sections for identification of traps, gravity, magnetics and bathymetric data may also be helpful.

Where thickness and character of rock sequences suggest adequate hydrocarbon source potential, quality of seismic data is critical. Migrated depth sections may be needed to evaluate faults as migration paths. Maps on key horizons may be necessary to document local structure and trapping configurations. Regional maps to ascertain relief on pinchouts may be needed to evaluate potential stratigraphic traps. Site proponents and JOIDES scientific panels are urged to select sites off structure, where desired objectives can be reached, even if this action means an increase in drilling depth.

C. Known Oil and Gas Occurrences

In planning a drilling leg, all information on oil and gas wells or seepages close to proposed sites, both on and offshore, must be obtained. This information is vital on continental margins. Shallow piston cores near proposed sites may provide information on hydrocarbon occurrences in surface sediments. Petroleum companies who hold or have held concessions in the general vicinity are good sources of information of this type. It must be noted that presence of an industry "dry hole" near a proposed site does not equate with a complete absence of hydrocarbons at that site.

D. Abnormal Pressures

Areas and stratigraphic intervals containing fluids under greater-than-normal hydrostatic pressure should be avoided because of their common association with oil and gas and their tendency to cause blowouts. Presence of under-compacted shale is a warning that fluids may be encountered at more than normal hydrostatic pressure. An under-compacted shale is one in which fluid expulsion has not kept pace with increased fluid pressure, so that formation fluids in the shale and associated sands are not only under hydrostatic pressure but also bear part of the weight of the overlying rock column. Fluid pressures in such shales may also have a component of pressure generated internally by buoyant forces related to contained gas. Pressure-compacted shales may be identified by decreases in their interval velocities related to their abnormally high fluid content. They may also appear in seismic sections as distorted, convoluted reflections. Under-compacted shales may show up on gravity profiles because of their lower densities. Absence of velocity inversion does not preclude abnormal formation pressure, nor does its occurrence always result from an under-compacted shale section. Nevertheless, drill sites at which marked velocity inversions are detected should be avoided unless the inversion can be related to some other lithologic change.

E. High Geothermal Gradients

Heat flow data should be acquired at prospective drill sites to assess the depth at which petroleum generation may take place and because higher temperatures are commonly associated with abnormally high pressures and hydrocarbon accumulations.

F. Water Depth

Blowout danger diminishes greatly with increased water depth. Violent surface blowout may occur in water depths as great as 500 m, but there is little likelihood that such blowout danger exists in depths of 2,000 m or more. Quiet escape of oil or gas into the sea, with consequent risk of pollution and loss of valuable hydrocarbons, can occur while drilling in any water depth.

G. Significance of Gas Hydrates to Safety of Drill Sites

Gas hydrate is the common name for the water clathrate of methane—$CH_4 \bullet 6H_2O$. This ice-like substance can precipitate as a solid phase in deep-sea sediment when sufficient amounts of dissolved methane are present and the pressure-temperature conditions are appropriate. Because of increased temperature with depth in sediments, the clathrate structure is stable only within a limited thickness in the upper part of the sediment. At some depth beneath the sea floor (depending on pressure and gas composition), the temperature will be too high for gas hydrates to exist. A method to calculate the depth to the base of the methane hydrate stability zone in marine sediments is given in Appendix 2E.

Gas hydrates have been physically recovered from cores on DSDP Legs 66, 67, 76 and 84, and on ODP Legs 112, 127 and 131. Occurrence of gas hydrates was suspected but not confirmed at several other sites. In all cases where gas hydrates have been recovered by DSDP/ODP coring, the composition has been relatively pure biogenic methane with low salinity water in the solid phase.

Indirect evidence for gas hydrate occurrence in deep sea sediments is the bottom-simulating seismic reflection (BSR) that is sometimes present at the base of the gas hydrate stability zone. Previous safety advice was that drilling should not continue beneath the theoretical depth of methane hydrate stability in sediment where gas hydrate was present. This advice was based on the assumption that the BSR and the base of the gas hydrate stability zone are associated with significant amounts of free gas, possibly at high pressure, beneath a gas-hydrate seal.

Subsequent reinterpretation of marine gas hydrate phenomena indicates that quantities of free gas beneath the gas hydrate stability zone should be minor, and that the gas pressure should be controlled at hydrostatic by equilibrium with gas hydrate. Based on this reinterpretation, PPSP has approved drilling beneath visible BSR's *in geologic settings that are otherwise considered safe from the standpoint of potential drilling hazards associated with hydrocarbon accumulations.*

H. Weather

Year-round weather data are essential for choosing optimum times for drilling particular areas. The JOIDES Planning Committee (PCOM) and the Science Operator must be familiar with weather and sea conditions for proposed drilling legs so that scheduling can be adjusted to minimize hazards related to weather. In high latitudes, information on sea ice conditions is also critical.

I. Political Considerations

Different countries have different standards regarding pollution prevention. It is not PPSP's responsibility to resolve problems of this nature, because their solution involves international law and top level policy-making on behalf of ODP. PPSP does, however, ask that PCOM, the Science Operator, and Co-Chief Scientists supply information on distances of various sites from shore and probable political jurisdictional control of each site. This information enables PPSP members to call attention to possible political difficulties of which, through their broad experience, they may be aware.

Precautions in Planning Drilling Programs for Individual Holes

A. Depth of Penetration

A subbottom penetration to no more than 50m or to refusal of the advanced piston corer, even on a structure, is not considered hazardous because hydrocarbons at high pressures are unlikely at such shallow depths in relatively soft sediments. Deeper penetrations should depend on assurance that a dangerous combination of hydrocarbon sources, traps and reservoirs does not exist.

B. Coring Program

The standard policy for ODP drilling is continuous coring of all holes. Deviation from this policy requires PCOM approval to avoid science omissions and PPSP approval to avoid safety risks. Examination of cores and fluids obtained from the hole is the only means available for monitoring hydrocarbons and other indications of potential hazards.

C. Re-entry

The greater penetration depth potential provided by re-entry capabilities increases the chance of encountering hydrocarbon reservoirs and blowouts. Re-entry capability, however, may aid pollution prevention and safety assurance by facilitating use of logs before reaching total depth in a hole and by providing a means of testing cement plugs.

Measures for Early Detection and Anticipation of Hydrocarbons During Drilling

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

Constant vigilance with regard to detection of hydrocarbons and possible approach to hydrocarbon accumulations should be observed throughout drilling at every site where hydrocarbon occurrence is a possibility. Routinely, visual examination should be made of each core as soon as it is removed from the barrel. A designated member of the scientific party should examine all cores and fluid recovery for hydrocarbon shows; shows that appear to be significant should be immediately analyzed by qualified personnel. Appropriate samples should be taken and quantitatively analyzed for content of dissolved hydrocarbon gases. Examination by qualitative solvent extraction, ultraviolet fluorescence and pyrolysis should also be made to detect presence of migrated hydrocarbons.

Principal questions to be answered are: have hydrocarbon-bearing strata been penetrated that could pollute ocean waters or adjacent strata or cause hazards to safety? what warning signals regarding safety and pollution prevention can be found that bear on the advisability of discontinuing drilling?

Significance of hydrocarbons shows can only be evaluated properly in light of other factors:

1. general geologic background;
2. lithologic and lithogenetic character of the section penetrated and to be penetrated;
3. petroleum indications in the region;
4. records of other drilling in the vicinity;
5. probability of reservoir rocks;
6. probability of source rocks;
7. probability of evaporites and under-compacted shales;
8. temperature-pressure conditions with respect to gas hydrate formation;
9. probability of traps;
10. water depth; and
11. proposed drilling and coring program.

The best guideline is that drilling should be stopped if hydrocarbons or hydrocarbon indications are encountered that suggest presence of substantial accumulations of gas or oil.

Several features of the chemical composition of hydrocarbons detectable in cores or fluid samples contribute to proper understanding of subsurface processes and bear on decisions regarding where to drill and cessation or continuation of drilling. Identification of chemical and physical properties of any gas, liquid or solid petroleum substance is critically important to recognition of presence or possibility of dangerous accumulations. Composition of gas shows may enable distinction between biogenic gas and thermogenic gas that has leaked upward from an underlying oil and gas accumulation. Gases associated with liquid petroleum commonly have C_2-C_5 (ethane through pentane) content of several percent of total hydrocarbons in the gas phase. In many cases, ethane content shows erratic increases on an exponential scale with increasing penetration depth. Ethane appears to result from slow, *in situ* generation by thermochemical processes beginning at relatively low, near-surface temperatures and increasing with depth. Bacteria may also be capable of generating minor amounts of ethane. In any case, it is primarily quantity of hydrocarbon gas and possibility of accumulation and trapping that pose potential danger. Origin and composition are of secondary importance.

The degree of generation of petroleum from source rocks is primarily related to the temperature that the source rocks have experienced. Thermal maturity can be estimated from chemical composition of sediment gas, distribution of solvent-extractable hydrocarbon constituents, pyrolysis assay, and color and reflectance of organic particles. (Use of these techniques to determine maturation is discussed in Tissot and Welte, 1984, p. 515-540.)

Level of maturity must be known in order to evaluate significance of hydrocarbon shows. Presence of typical crude or wet gas in a sedimentary sequence containing immature organic matter implies a migration pathway from a deeper, hotter source. In contrast, sequences rich in organic matter sometimes locally contain immature hydrocarbons. It may be difficult to distinguish between immature bitumen and biodegraded, mature oil residue.

It is important to make some estimate of quantity of hydrocarbons associated with a given amount of sediment. A quantitative estimate of petroleum (gas, liquid or solid) is critical in deciding whether hydrocarbons are migrated or indigenous. Abrupt changes in hydrocarbon contents of cores could signal presence of an accumulation at greater depth.

PPSP recommends that drilling be stopped if mature migrated hydrocarbons are detected. It is possible that special geologic information might mitigate dangers of a spill or blowout to the extent that drilling could be resumed. However, a decision to resume drilling should only be made after thorough evaluation by responsible shipboard personnel and consultation with shorebased ODP operations.

B. Continuous Observation of Drilling Rate for Overpressure Detection

Drilling rates should be continuously monitored. Under-compacted shales are often capped by relatively hard, cemented layers; sudden increases in drilling rates could signal entry into overpressured, under-compacted shales. The Pressure Core Sampler (PCS) may be used to detect over-pressured shales and gas hydrates when and where they are expected.

C. Well-logging

A principal value of routine logging (electrical, sonic and nuclear) is to provide a continuous record of the hole through intervals that are not cored or where core recovery is poor. It is advisable for pollution prevention and safety purposes to log each stage of penetration as drilling proceeds. Logs reveal potential reservoirs, anomalous temperature gradients and source horizons and should be a "must" for holes requiring deep penetration into potential hydrocarbon-generating sections. The ODP logging program of Lamont-Doherty Geological Observatory (LDGO) will also provide invaluable records of holes for future reference. See the ODP Wireline Logging Manual (2nd edition), 1990, of the Borehole Research Group (LDGO) for further information on logging capabilities.

Measures for Coping with Fluid Flow Encountered During Drilling

A. Drilling and Early Abandonment Practices

Rapid pipe or tool movements that may swab fluid into the hole or fracture formations should be avoided. If hydrocarbons are detected or anticipated in substantial quantities, drilling should be stopped and the hole plugged.

B. Plugging and Abandonment Procedures

1) With cement

The hole should be filled with viscous gel barite mud of 75 lb/ft^3 weight, allowing extra volume for hole enlargement and loss by displacement. The hole should be filled to the uppermost competent layer and a cement plug spotted. A minimum sized plug should be 200 sacks of 12-15 lb/gal. Where possible, a plug catcher or calibrated displacement tanks should be used in placing the cement.

If hydrocarbons are indicated, and the hole has penetrated semi-consolidated or consolidated rocks, proper placement of cement should be confirmed by probing with the drill string or sampling the cement with the core barrel. The cement plug should be calculated to be at least 15 m and preferably 30 m in length.

2) Without cement

The hole should be filled with viscous gel barite mud of 75 lb/ft^3 weight, allowing extra volume for hole enlargement and loss during displacement.

C. Standard Abandonment Procedures

Holes drilled in consolidated or semi-consolidated rocks on the continental shelf, slope or rise should be plugged with cement. Holes drilled in unconsolidated sediments in which shows of oil or gas occur should be filled with mud. Holes on the deep ocean floor in which no shows are encountered or holes in igneous rocks may be abandoned without plugging.

Appendix 1: Guidelines for Safety Reviews

A. Introduction

Both the JOIDES Pollution Prevention and Safety Panel (PPSP) and the Ocean Drilling Program Safety Panel (ODPSP) give advice and make recommendations that are incorporated in the final decision on whether a specific site will be drilled. This decision is made in the course of a safety review. In questioning site proponents, reviewing data and discussing problems, there is no distinction between the two panels. However, panels arrive at their decisions independently and unless their conclusions are identical, the more conservative decisions and advice are followed.

Co-Chief Scientists, during the safety review, document safety conditions extant at proposed sites and the safety panels examine these data. Failure by Co-Chief Scientists to meet their responsibility of providing adequate data for review will result in rejection of a drill site by the safety panels.

B. Procedures

Safety panel reviews vary from leg to leg, depending on geological setting of drill sites and quality and quantity of available data. The following guidelines provide the overall scope of the review, that must include a synthesis of geological, geochemical and geophysical data at each site.

Material for the review is presented in two stages. The first consists of material mailed to panel members at least two weeks prior to the review meeting. This material should acquaint members with location, structure, stratigraphy and potential safety problems at drill sites and must include Safety Review Check Sheets (Figure 3) for each site. This mailed documentation allows panel members to search their own files for information on potential hydrocarbon and other hazards at proposed sites. The second stage is formal presentation of all pertinent data at the Safety Review Meeting. Avoiding reference to data that may indicate drilling hazards in the course of this presentation can be a significant deterrent to panel approval. Bringing such data into the open, where its merits can be judged in light of overall safety aspects of a site, is the best policy for Co-Chief Scientists presenting data. It should be noted that proposals to drill on structural highs will generally be amended with recommendations to relocate the site on the flank of the structure. The safety panels are also inclined to relocate drill sites to intersections of seismic lines, especially where sedimentary sections are thick and where traps are likely to occur.

Much of the data needed for safety reviews is also required to support submission of a mature drilling proposal. Data which should be submitted to the ODP Site Survey Data Bank and submittal formats are described in the revised ODP Proposal Submission Guidelines, *JOIDES Journal*, v. 18, no. 1, February 1992, p. 29-33, and are periodically updated in that journal.

C. Schedule for Safety Review

Program schedule requires safety reviews at least six months before a drilling leg begins. The review can be conducted even earlier, as this may allow collection of additional data at rejected sites or new data for alternate sites.

D. Safety Previews

If, early in planning, proponents of a drilling leg anticipate serious safety concerns, they should request a safety preview. This entails submission of initial reconnaissance information and allows a preliminary assessment of problems before major commitments of time and money are made. The preview should be done at a scheduled Safety Review Meeting. The matter should be discussed with the PPSP chairperson in order to make necessary arrangements.

E. Safety Panel Recommendations

At the Safety Review Meeting, the panels will advise Co-Chief Scientists that a site: a) is approved as proposed; b) should be moved to safer location that is still compatible with scientific objectives; or c) is rejected due to inadequate data or inherent risk. The safety panels may recommend a preferred order of drilling if safety is a factor, and also specify any conditions of approval, such as maximum depth of penetration, or special monitoring requirements.

F. Documentation For Safety Review

Documentation required for material mailed to panel members prior to review meeting:

1. Regional map showing bathymetry, latitude and longitude, nearest land areas and proposed site locations.
2. Track chart showing proposed sites and specific lines or line segments included for review.
3. Cross-tied seismic reflection lines of sufficient length and detail to define closures. The following annotations should be included on these lines:
   a) site number, location and penetration depth;
   b) traverse direction;
   c) horizontal scale in kilometers;
   d) vertical scale in seconds or meters;
   e) course changes;

Revised January 1991

SAFETY CHECK SHEET
JOIDES POLLUTION PREVENTION AND SAFETY PANEL

1) Basic site information.

Leg:	*Site designation:*	*Latitude:*	*Longitude:*
Water Depth (m):	*Distance from land (n. mi.):*	*Jurisdiction:*	
General location or geomorphic province:			
Probable thickness of sediments (m):	*Proposed total penetration (m):*		

2) Upon what geophysical and/or geological data was this site selection made?

Multichannel seismic lines:
Single channel seismic lines:
DSDP/ODP holes:
Piston cores:
Other:

3) What is your proposed drilling program?

____

____

____

4) What is your proposed logging program?

____

____

____

Figure 3a. Safety Check Sheet, p. 1.

Site __________, page 2

5) From previous DSDP/ODP drilling in this area, list all hydrocarbon occurrences of greater than background levels. Give nature of show, age and depth of rock:

6) From available information, list all commercial drilling in this area that produced or yielded significant shows. Give depths and ages of hydrocarbon-bearing deposits:

7) Is there any indication of gas hydrates at this location?

8) Is there any reason to expect any hydrocarbon accumulation at this site? Please comment.

9) What "special" precautions will be taken during drilling?

10) What abandonment procedures do you plan to follow?

Summary: What do you consider to be the major risks in drilling at this site?

Figure 3b. Safety Check Sheet, p. 2.

JOIDES Safety Review Check Sheet

GRAPHIC SUMMARY,

Sub-bottom depth(m)	Key reflectors, uncomformities, faults, etc.	Age	Assumed velocity (km/sec)	Lithology	Paleo-environment	Average rate of sediment accumulation (m/My)	Comments
			1.50	(Water)			
0	Sea floor	Pliocene to Recent	1.58	Interbedded sand, silt and clay	Distal turbidites in basinal setting	60	Upper stratified seismic interval
200							
	???	Late Miocene	2.10	Diatomaceous clay	Hemipelagic basinal setting	100	Basal stratified seismic interval??
400	???	Late Miocene	2.20	Clay and diatomaceous clay	Hemipelagic basinal setting	100	Upper transparent seismic interval?
600	AB'	Late Miocene	2.50	Basalt and volcanoclastics	Back-arc/ marginal sea		Acoustic basement

AB' – Acoustic Basement

Figure 3c. Safety Check Sheet, p. 3.

f) identification of important reflections; and

g) cross-line intersection points.

Seismic events should be legible to the depth of proposed penetrations. Seismic data may be presented as records or photographic prints. Suitable annotated negatives of prints must be sent to the ODP Site Survey Data Bank.

4. Sketch of major structural elements, sediment thicks and thins, and areas of distinctive reflection character.
5. Safety review check sheets. Material submitted for each site should be indexed and annotated to enable ready identification of structural features, line locations, line directions, wells, grab samples, cores, etc.

At the Safety Review Meeting, Co-Chief Scientists should present scientific objectives of the leg using regional maps, sections and published material as appropriate. This presentation should provide a comprehensible regional picture within which scientific objectives and safety hazards at each site can be evaluated. Co-Chief Scientists will present geologic characteristics and potential hazards for each site. Required items for all sites include:

1. All available bathymetric data.
2. Track charts with locations of geological, geophysical and geochemical data; seismic lines to be reviewed; site locations.
3. Structure maps, sedimentary thickness maps and maps of estimated depth to base of clathrate horizons.
4. Seismic reflection data sufficient to defend the safety of each site. In the event a site is moved, it is necessary to base the new location on additional seismic data. Documentation should be available for alternate locations. Drilling below the depth of resolution of seismic data will not be approved. Interval velocity information should also be provided.
5. Seismic refraction, gravity and magnetic data.
6. Hydrocarbon occurrences at nearby boreholes or exploration wells should be tabulated. Oil companies should have been encouraged to release such data. Potential source rocks should have been identified and mapped.
7. International jurisdiction and extent of nearby oil leases.
8. Lithologic descriptions of available cores and dredges, together with existing analyses of sediments and bottom water for presence of hydrocarbons.
9. Regional geologic maps and cross-sections for consideration of possible relationship of onshore and offshore geologic sections. Reservoir data should also be made available, if possible.

Appendix 2: Hydrocarbon Monitoring

A. Introduction

Two general procedures are relied upon to prevent ODP from drilling sediments that might contain hydrocarbon accumulations. The first is the site selection and review process, in which proposed drill sites with geological factors conducive to hydrocarbon accumulation are either eliminated from the drilling program or relocated to avoid possible safety problems. The second is regular monitoring of cores to insure that sediments being drilled do not contain greater than expected amounts of hydrocarbons. Shipboard personnel are faced with the practical problem of distinguishing "expected" or "normal" amounts of hydrocarbons, from "greater than expected" levels of hydrocarbon occurrence that could be cause for cessation of drilling. It is not possible to specify quantitatively amounts or proportions of hydrocarbons that would be cause for site abandonment under all conditions. Relatively small amounts of wet gas hydrocarbons could be cause for concern when coring in young, cold sediments overlying an older, possibly oil-generating sedimentary section. In contrast, evidence of slow *in situ* hydrocarbon generation should be expected when coring in organic matter-rich sediments at elevated temperatures.

B. Gas Analyses

The most common method of hydrocarbon monitoring used in ODP operations has been analysis of gas samples obtained from gas expansion pockets visible through clear plastic core liners. Gas composition is commonly expressed as C_1/C_2 ratio, and plotted versus depth below sea floor. A compilation of gas data from selected DSDP sites is shown in Figure 4. Although not now recommended by PPSP, a C_1/C_2 ratio of about 1000 was used as a working guideline for termination of drilling during earlier phases of DSDP. An updated compilation of gas analyses from more recent ODP drilling is shown in Figure 5.

Patterns of C_1/C_2 decreases with depth illustrated in Figures 4 and 5 represent a variety of geologic settings. C_1/C_2 can indicate proximity to a possible hydrocarbon accumulation, as shown on DSDP Leg 10, where Site 88 was drilled to within about 135 meters of the top of a salt dome in the Gulf of Mexico. High levels of ethane and other hydrocarbons (plus the subsequent carbon isotopic characterization of the methane) in Site 88 sediments clearly show that most of the gas has migrated from a deeper accumulation or source of thermogenic hydrocarbons. Sites 481 and 477 were drilled in the Gulf of California, where igneous intrusions have generated hydrocarbons locally in organic-rich sediments. At other drilling sites, C_1/C_2 ratios reflect primarily temperature, and secondarily age and organic matter content of the sediment. The consistent relationship between C_1/C_2 and temperature suggests that in typical cases, C_{2+} gas has not migrated from some deeper source, but was generated *in situ* by early stages of low-temperature, thermal decomposition of organic matter.

The relationship between C_2 content of microbial methane "gas shows" and sediment temperature at the depth of the gas show can be used as one criterion to evaluate the

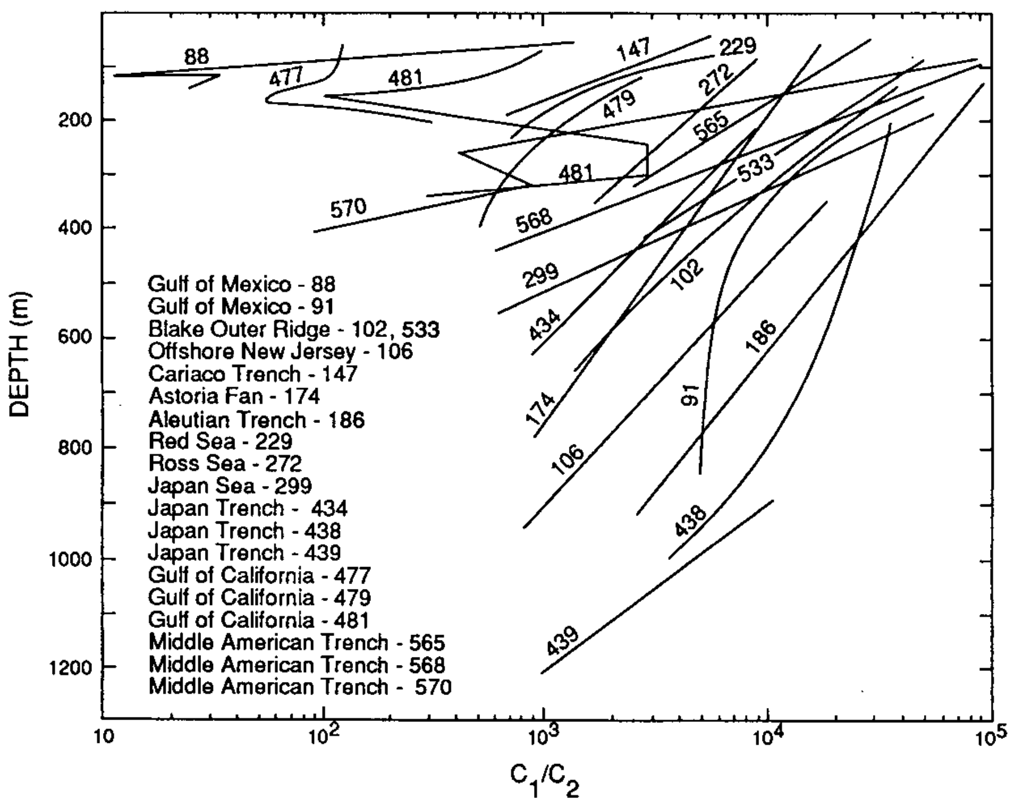


Figure 4. Methane to ethane ratios (C_1/C_2) of gas pocket (vacutainer) samples with depth of burial for selected DSDP sites. [Constructed from *Init. Rpts. DSDP* series, 1973-1985, vols. 10-85: Washington (U.S. Govt. Printing Office).]

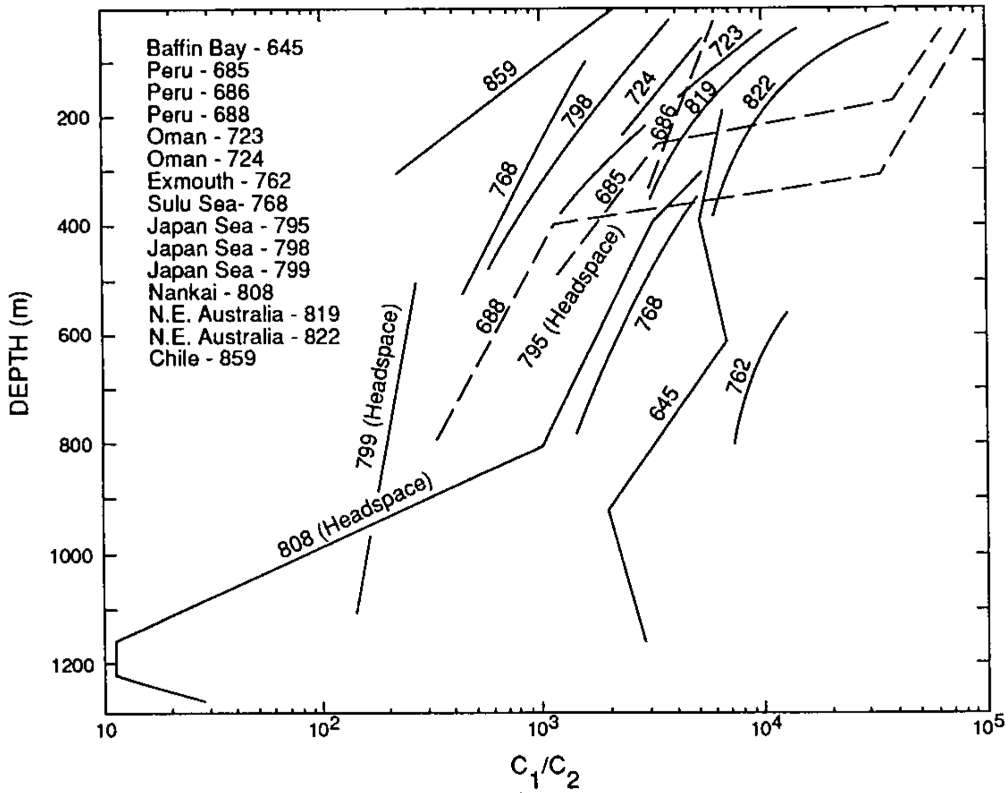


Figure 5. Methane to ethane ratios (C_1/C_2) of gas pocket (vacutainer) samples with depth of burial for selected ODP sites. [Constructed from *Proc. ODP, Init. Repts.*, 1986-1993, vols. 101-141: College Station, TX (Ocean Drilling Program).]

"normal" vs. "anomalous" nature of such hydrocarbon occurrences. A plot of C_1/C_2 ratios versus temperature is shown in Figure 6, with a pattern that approximately separates "anomalous" from "normal" C_1/C_2 ratios. Also shown by the two lines is the approximate influence of different levels of organic carbon content.

Use of Figure 6 as a hydrocarbon monitoring guideline requires estimates of sediment temperature. The need for temperature information to evaluate gas shows properly means that regular use of the heat flow probe or logging tools will be required in gassy sediments. Besides direct temperature measurements, the inferred depth to gas hydrate bottom-simulating reflections can also be used to estimate temperature gradient.

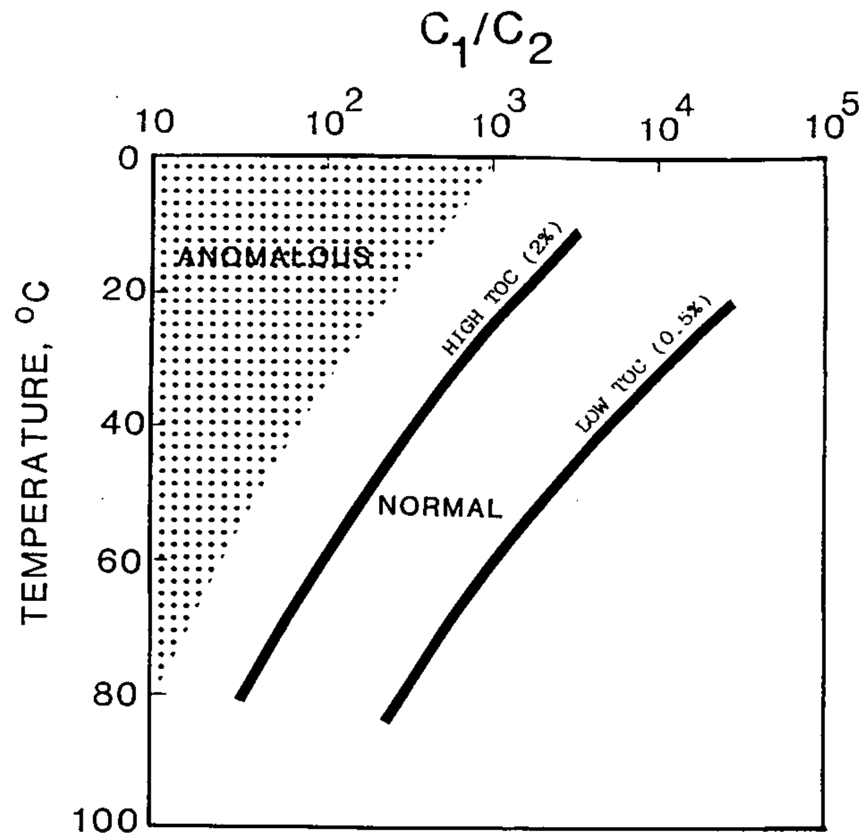
In addition to gas pocket or vacutainer gas samples, "headspace" gas analysis is now used routinely for hydrocarbon monitoring of cores. Headspace and vacutainer techniques generally give comparable results in sediments where there is a large background of microbial methane present. When active methane generation is not occurring, the headspace gas technique gives much lower C1/C2 ratios, and the guidelines discussed above cannot be used. In the absence of a high background concentration of microbial methane, other hydrocarbon monitoring techniques such as Rock-Eval and solvent extraction/gas chromatography (see below) should be used.

Hydrocarbon monitoring techniques are designed to recognize small quantities of migrated hydrocarbons. It should be kept in mind that the quantity of gas present in the sediments being drilled is as important as the source of the gas. In the absence of a functioning pressure-core sampler (PCS), there is no method for accurately estimating the quantity of gas associated with a given quantity of sediment. With the advent of a functioning PCS and shipboard systems for degassing confined core samples, efforts should be made to measure the quantity of gas associated with a given quantity of sediment. A qualitative scale for rating the amount of gas in cores, called Gas Quantity Factor (GQF), has been developed by Glen Foss (Supervisor, Drilling Operations, ODP/TAMU). The GQF scale is useful as a guide, based on past observations:

- GQF 0 - No noticeable degassing or detectable hydrocarbons in core tube (vacutainer) samples.
- GQF 1 - Detectable hydrocarbon gas, but insufficient for reliable analysis. No notable pressure, separations or bubbling.
- GQF 2 - Sufficient hydrocarbon gas for analysis of core tube samples. Widely scattered bubbling and/or separations.
- GQF 3 - "Frying" or "chirping" sounds of gas bleeding from indurated cores. Slight bulging of end caps in storage rack. Minor checking (i.e., incipient cracking) and cracking in softer cores.
- GQF 4 - Pronounced bubbling of gas from core on retrieval. Numerous small separations in soft cores. Strong bulging of end caps.
- GQF 5 - Numerous large separations in soft cores. End caps blown off. Small amounts of soft core extruded from sections on rack.
- GQF 6 - Indications of pressure before opening core barrel—water forced out through check valve at top of barrel. Pronounced expansion of soft core on removal from barrel.
- GQF 7 - Core catcher forcibly blown off. Very large gas-filled voids in core liner.

These GQF guidelines do not necessarily indicate safe operational limits. However, GQF can be used to estimate trends of relative gas content with depth. The last two

Figure 6. Gas composition (as C_1/C_2) versus temperature of sediment from which the gas sample was obtained in DSDP/ODP coring operations. The field labelled "Anomalous" represents gas composition suggestive of migrated thermogenic hydrocarbons.



stages (GQF 6 and 7) may indicate presence of gas hydrates in cores.

C. Rock-Eval Pyrolysis

"Rock-Eval" pyrolysis data are commonly used to quantify a sample's hydrocarbon generation potential and the nature of its kerogen, and to estimate its level of thermal maturity. "Rock-Eval" data can be used to identify heavy hydrocarbon oil shows (Espitalie et al., 1984).

A direct measure of the quantity of oil-like material is provided by the S_1 (free hydrocarbons) value. Marine sediment samples with S_1 values of 1.0+ mg HC/g rock are unusual. This yield would be equivalent to 35 barrels oil/acre-foot. Absolute S_1 values alone, however, should not be used as a direct indication of the presence of migrated or *in situ*-generated thermal hydrocarbons. Organically enriched sediments (TOC > 2.0 wt.%) may display S_1 values greater than 1.0 mg HC/g rock. For ODP safety considerations, such samples should undergo further analysis (solvent extraction and gas chromatography) to determine if they exhibit characteristics of thermally mature hydrocarbons. Identification of thermally mature hydrocarbons should be considered reasonable grounds for termination of drilling.

The "Rock-Eval" system provides other methods to identify the presence of non-indigenous hydrocarbons. These include the relationship between T_{max} (temperature of peak pyrolytic hydrocarbon generation) and the Production Index (S_1/S_1+S_2) and, as a second independent check, the S_1/TOC ratio.

Hydrocarbon shows are suggested when a sample displays a depressed T_{max} value relative to its Production Index. A suggested correlation between T_{max} and the Production Index is presented in Figures 7 and 8. In general, if T_{max} is less than 440°C and the Production Index is greater than 0.20, the presence of nonindigenous hydrocarbons (i.e., migrated products or contaminants) is suggested (Figure 8). This interpretation scheme is based on the work of Clementz (1979), who suggested that heavy hydrocarbons will bleed-over into the S_2 (pyrolytically-generated hydrocarbons) peak, resulting in a minor increase in the S2 yield and a significant reduction in the Tmax value.

A hydrocarbon show is also suggested when the S_1/TOC ratio is greater than 1.5 (Figure 9). Such elevated values suggest that the quantity of hydrocarbons is in excess of that which is typically associated with indigenous organic matter. It is based on previously established relationships between C_{15}+ extractable hydrocarbons and total organic carbon content (Le Tran et al., 1974). Vacutainer, headspace and Rock-Eval pyrolysis results should all be recorded on standard safety log sheets (Figure 10).

Safety and pollution prevention considerations require that drilling be terminated if either or both of the indices described above suggest presence of migrated hydrocarbons. Although neither ratio necessarily indicates presence of reservoired hydrocarbons, they do suggest presence of an active hydrocarbon system capable of generating and expelling petroleum. Inadvertent penetration of a reservoir unit in such a system could lead to serious pollution and safety problems.

D. Solvent Extraction and Gas Chromatography

When cores are suspected to contain migrated petroleum (because of fluorescence, anomalous C1/C2 ratios or other evidence), it may be useful to determine if the extractable organic matter in the cores has a molecular distribution that resembles petroleum. This can be done by extracting a small amount of the dried sediment with hexane, concentrating the extract solution to a small volume, and analyzing the extract by high-resolution gas chroma-

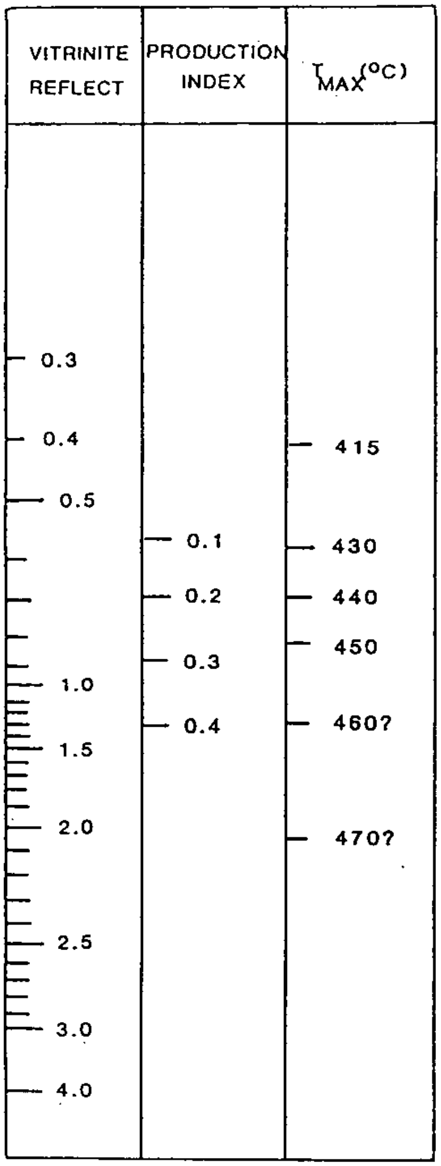


Figure 7. Correlation of vitrinite reflectance, Production Index and T_{max} (°C).

tography. This procedure is time-consuming (about 1 hour), and should be considered only as a means to resolve specific questions related to continuation or termination of drilling. A major problem is the time required to remove water from the sediment. Sediment must be dried rapidly without loss of high molecular weight hydrocarbons. Standard methods for water removal are: 1) freeze drying, 2) vacuum oven drying at 40°C, or 3) oven drying at 60°C.

About 5 g of pulverized dried sediment should be shaken and sonicated with 10 ml of chromatographically pure *n*-hexane. After

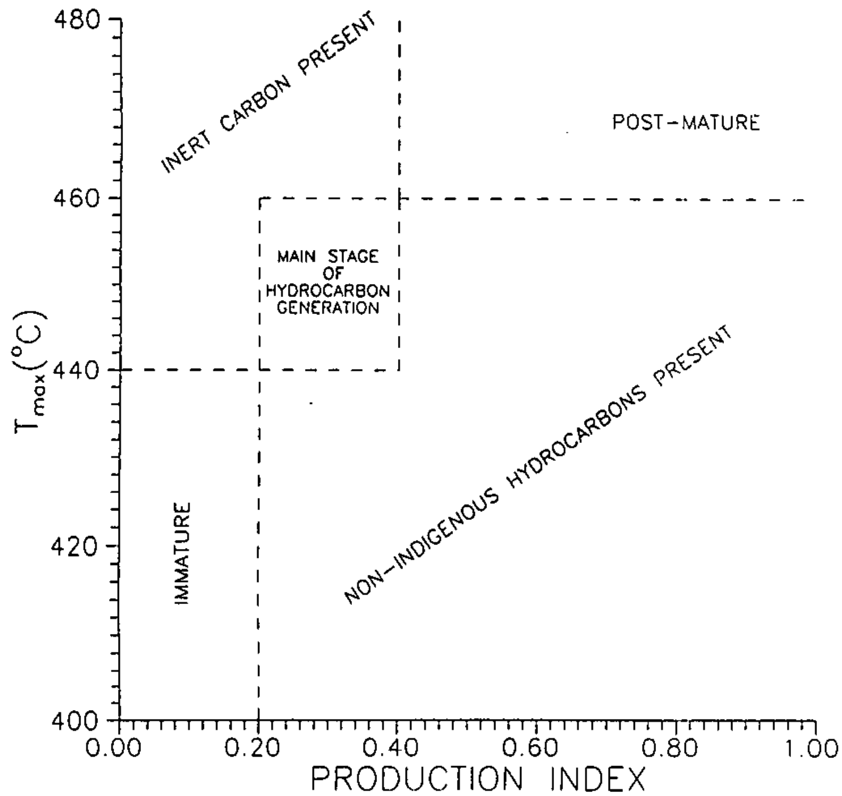


Figure 8. Production Index versus T_{max}.

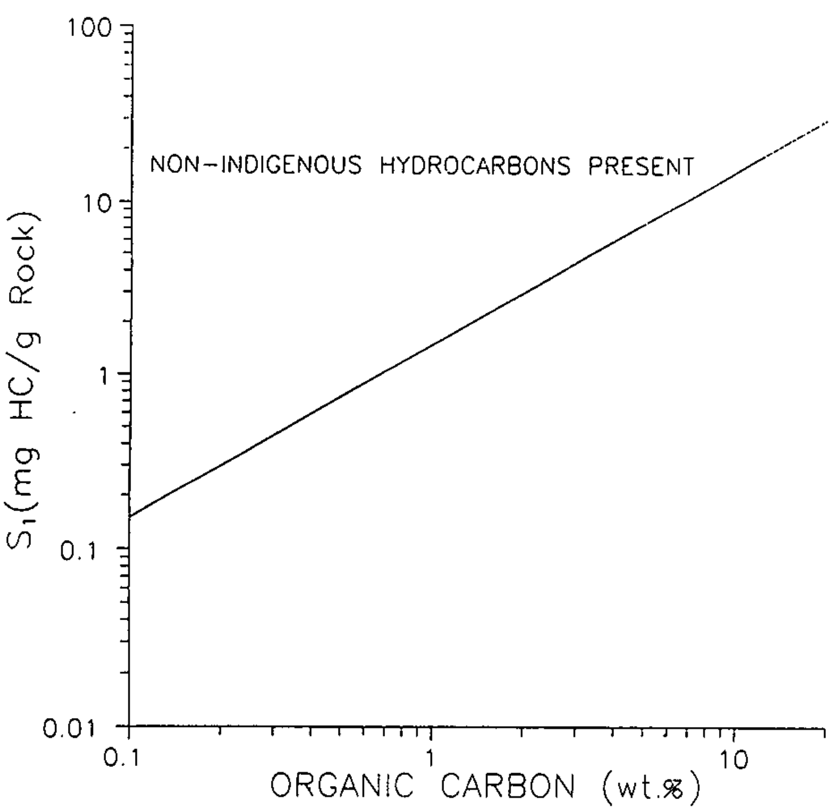


Figure 9. Organic carbon versus S_1.

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SAFETY LOG-SHEET

LEG:
SITE:
HOLE:

WATER DEPTH (m):
SEAFLOOR TEMPERATURE (°C):
GEOTHERMAL GRADIENT (°C/m), assumed: measured:
CALCULATED BASE OF THE HYDRATE STABILITY ZONE (m):

	min	max	depth of max concentration
TOC (%)			
Gas content (GQF)			
Vacutainers C1(ppm) C2(ppm) C3(ppm)			
Headspace C1(ppm) C2(ppm) C3(ppm)			
RockEval S1 S2 PI Tmax			

Comments:

Figure 10. Standard Safety Log Sheet.

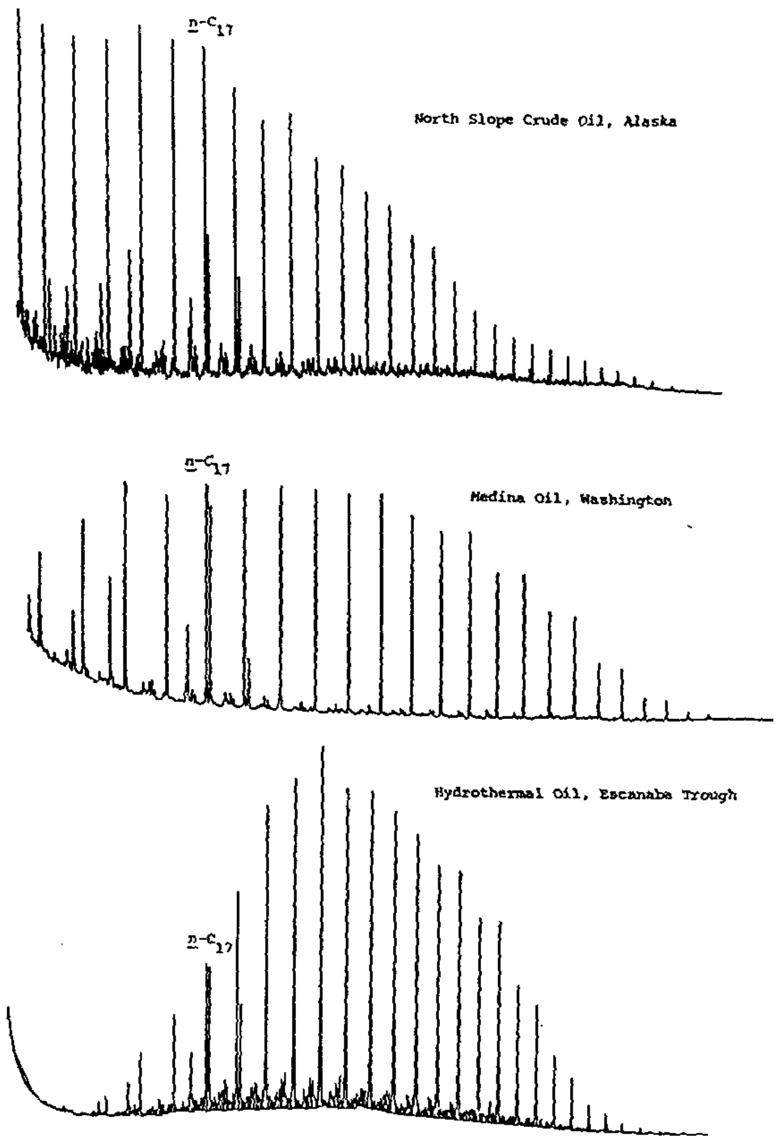

Figure 11. Gas chromatograms of crude oils analyzed using hexane extraction.

filtration through glass wool, the extract solution should be heated (40°C) and concentrated under flowing nitrogen or helium to a volume of about 0.1 ml. Using a syringe, about 1 µl of concentrated extract should be injected into a high resolution gas chromatograph, and the resulting chromatogram interpreted relative to the possible presence of petroleum. Some examples of crude oils analyzed by this technique are shown in Figure 11. A procedural blank using about 10 ml of *n*-hexane should be run to determine the expected background.

An alternative to the solvent extraction/gas chromatography procedure described above is an instrumental technique that vaporizes hydrocarbons from sediment and analyzes them by gas chromatography. This commercial apparatus, called the Geofina Hydrocarbon Meter, has recently been installed onboard *JOIDES Resolution*. Background information for use of this instrument and interpretation of results should be available as part of shipboard laboratory procedures.

E. Depth to the Base of the Gas Hydrate Stability Zone

Shipboard personnel should be aware of the depth to the base of gas hydrate stability when gassy sediments are being cored. Careful observations (including pressure core samples, if possible) should be made near this depth to help improve understanding of gas hydrate phenomena, both for drilling safety and scientific purposes.

To provide consistency in estimates of depth to the base of gas hydrate stability, a numerical calculation method should be used rather than published phase diagrams. Seismic velocity and reflection time can be used when BSR's are present at or near the drill site. The BASIC computer program shown in Figure 12 calculates the base of hydrate stability from:

- water depth (meters);
- bottom water temperature (°C);
- geothermal gradient (°C/km);
- hydrostatic pressure gradient (10.17 kilo pascals per meter (kPa/m)).

Experimentally determined methane-water hydrate P-T equilibrium is governed by the equation

$$\ln P = A - B/T$$

where P is pressure in kPa and T is temperature in degrees Kelvin. A and B are constants with values of 38.53 and 8,386.8 (respectively) for the pressure range 2,505 to 11,556 kPa, and 46.74 and 10,748.1 for the pressure range 11,556 to 80,000 kPa. This calculation is highly sensitive to the geothermal gradient estimate, with ±0.1°C uncertainty causing about ±1% variation in the total (water + sediment) depth estimate.

The program shown runs on any version of BASIC, which is usually included with MS-DOS on IBM-compatible personal computers. To use this program, BASIC must

```
10 PRINT TAB( 6)"DEPTH TO BASE OF GAS HYDRATE STABILITY"
20 INPUT "WATER DEPTH, METERS                     ";D
30 INPUT "BOTTOM WATER TEMPERATURE, DEG C        ";TB
40 INPUT "GEOTHERMAL GRADIENT, DEG C/KM          ";DT
50 FOR Z=1 TO 2500 STEP 1
60 LET A=LOG(10.17*(D+Z))
70 IF A>9.355001 THEN GOTO 120
80 LET B=38.53-(8386.8/((TB+(Z*DT/1000))+273.15))
90 IF A<B THEN PRINT"BASE OF GAS HYDRATE STABILITY =";Z"METERS BELOW SEA FLOOR"
100 IF A<B THEN GOTO 180
110 NEXT Z
120 FOR Z=1 TO 2500 STEP 1
130 LET A=LOG(10.17*(D+Z))
140 LET B=48.74-(10748.1/((TB+(Z*DT/1000))+273.15))
150 IF A<B THEN PRINT"BASE GAS HYDRATE STABILITY =";Z"METERS BELOW SEA FLOOR"
160 IF A<B THEN GOTO 180
170 NEXT Z
180 END


RUN
     DEPTH TO BASE OF GAS HYDRATE STABILITY
WATER DEPTH, METERS                  ? 5000
BOTTOM WATER TEMPERATURE, DEG C      ? 2.5
GEOTHERMAL GRADIENT, DEG C/KM        ? 25
BASE GAS HYDRATE STABILITY = 1011 METERS BELOW SEA FLOOR
```

Figure 12. Program for calculation of base of gas hydrate stability.

be loaded into memory by typing BASIC or GWBASIC at the DOS prompt. The "OK" prompt appears when BASIC is loaded. Type lines 10-180 as shown and SAVE (F4 key) under an appropriate name. To run the program, use the RUN command (F2 key), and enter the requested inputs. The ENTER key must be pressed after each of these operations.

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