SHIPBOARD ORGANIC GEOCHEMISTRY
ON
JOIDES RESOLUTION

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PREFACE

"This will revolutionize geochemistry at sea," was the reaction of Dennis Graham, a chemistry technician with a long history in DSDP chemistry programs, after working--on the shakedown cruise, Leg 100 of the Ocean Drilling Program--in the Chemistry Laboratory of JOIDES Resolution. One of the main prerequisites for scientific advancement has always been the access to modern instrumentation, and the geochemical veteran cited above acknowledged the effort of ODP to provide a state-of-the-art laboratory for chemical work at the locus of interest: **the drill site.** Surpassing the main concern of shipboard organic geochemistry in previous phases of scientific ocean drilling, i.e. safety monitoring for hydrocarbons, geochemists onboard JOIDES Resolution are now able to analyze almost every property of sediments and rocks, ephemeral and resident, according to the modern analytical and data handling standards.

The following Technical Note is one of a series of three on geochemistry onboard JOIDES Resolution +). The demand for a concise description of tasks and supporting infrastructure for geochemical work onboard ship was the immediate reason for writing this series. Equally important was the desire to standardize methodology and to document geochemical work performed in the previous phases of scientific ocean drilling. They are intended to provide a guideline for shipboard geochemists, in order to facilitate their various duties.

The chemistry laboratory owes its tremendous potential to the advice and help of numerous individuals, who provided invaluable assistance in design and set-up. ODP acknowledges, in particular, the efforts of Drs. J.H. Brooks and M.C. Kennicutt II (Oceanography Department, Texas A&M University) in the planning stage; of Bradley Julson and Dennis Graham (ODP) for their activities toward setting up the laboratory in its present great shape; of Drs. Keith Kvenvolden (U.S.G.S., Menlo Park), Joris Gieskes (Scripps Institution of Oceanography), Kay Emeis (ODP), Mr. Thomas McDonald (Oceanography Dept., TAMU), and Ms. Gail Peretsman (ODP), who were responsible for setting up the methods and procedures for the chemistry laboratories and writing these reports; and of Ms. Katie Sigler, Ms. Gail Peretsman, Ms. Tamara Frank, Mr. Matt Mefferd, Mr. Larry Bernstein, and Mr. Bradley Julson, for their roles in the maintenance and operation of the chemistry equipment at sea. Without the efforts of all of the above persons, the chemistry at sea program would not have reached its present highly successful state.

+) Gieskes, J.M., and Peretsman, G., 1986. Water Chemistry Procedures aboard JOIDES Resolution. ODP Technical Note #5.
Kvenvolden, K.A., and McDonald, T.J., 1986. Organic Geochemistry on the JOIDES Resolution -- An Assay. ODP Technical Note #6.
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Philip D. Rabinowitz, Director

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I. INTRODUCTION

This manual was produced by the Ocean Drilling Program (ODP) to serve as a guide for the organic geochemist, and the chemistry technicians aboard JOIDES Resolution (SEDCO/BP 471). It treats aspects of the following shipboard chemistry program:

(1) sample collection and analysis for immediate safety decisions to avoid oil and gas accumulations in sediments drilled;
(2) the collection and preservation of samples for subsequent shorebased organic geochemical research; and
(3) the acquisition of organic geochemical data with the shipboard instrumentation.

This manual includes details on sampling procedures, data interpretation, and information on previous DSDP/ODP work. Routine sampling intervals, analytical procedures, and sample flow should follow these guidelines to ensure consistency from leg to leg.

A. DUTIES OF SHIPBOARD ORGANIC GEOCHEMIST

The success of the ODP organic geochemistry program depends to a large extent upon the interest and actions taken by the on-board representatives of the organic geochemical community. These scientists have five major duties:

1. to assist the Co-Chief Scientists and ODP Operations Superintendent in making proper decisions to avoid significant gas and/or oil accumulations during the drilling operations;
2. to ensure that the designated routine program for analyses of gases and organic carbon is maintained;
3. to assure collection of core samples that are frozen aboard ship, curated by ODP, and distributed to the scientific community on request;
4. to collect samples for their own research program and for the research programs of others, after such programs have been approved by the Co-Chief Scientists and ODP;
5. to provide organic geochemical reports for inclusion in the Hole Summaries and in the Proceedings of the Ocean Drilling Program volumes.

If there are questions concerning duties, procedures, or problems, contact:

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B. SAFETY

The primary responsibility of the shipboard organic geochemist is to provide, on the basis of his observations and expertise, advice concerning the probable risks of an uncontrolled release of petroleum hydrocarbons, that is, gas and/or oil. Impending risks to the ship and/or to the environment must be assessed, and the Co-Chief Scientists and ODP Operations Superintendent advised _in time that drilling can be terminated and the hole plugged before penetration of a hazardous depth interval._ The decision as to whether drilling is to be terminated and the hole abandoned rests with the Co-Chief Scientists and the ODP Operations Superintendent.

Organic geochemical procedures which can be performed quickly and reliably on shipboard are, at best, able to indicate possible risk. Such procedures should be interpreted in conjunction with geological, paleontological, and geophysical data. Although this function is the responsibility of the Co-Chief Scientists and the ODP Operations Superintendent, the shipboard organic geochemist assists with this multidisciplinary interpretation.

Generally, the hydrocarbon monitoring program consists of three main elements: (1) visual inspection, (2) gas analysis, and (3) pyrolysis. Other factors such as shale density and drilling breaks can be taken into account in the overall assessment of the potential danger in encountering significant quantities of hydrocarbons.

C. RESOURCES AVAILABLE TO THE ORGANIC ANALYST

We compiled this manual as a reference guide for shipboard organic geochemists, recognizing that the tasks on board may not fall into the respective expertise of specialized scientists. It is based upon the experiences of individuals who have participated in both DSDP and ODP operations.

Some of the resources aboard _JOIDES Resolution_ include:

1. the diverse backgrounds and scientific knowledge of the shipboard scientific party, including previous DSDP and ODP experience,
2. shipboard reports from previous DSDP and ODP legs, on file in the scientists' lounge,
3. a complete collection of DSDP _Initial Reports_, ODP Hole Summaries and/or _Proceedings of the Ocean Drilling Program_ volumes.
4. sophisticated shipboard equipment for geochemical studies with detailed operating/maintenance manuals,
5. the practical experience and instrumental expertise of the shipboard technicians. The technicians are very helpful in situations new to the shipboard scientist, and usually have had several legs worth of experience dealing with analytical and scientific problems.

D. INSTRUMENTATION FOR ORGANIC GEOCHEMISTRY

Modern instrumentation for organic geochemistry is available in the chemistry laboratory of JOIDES Resolution. These instruments include the following (Figure 1):

1) Hewlett-Packard 5890A Gas Chromatograph with Option 820 [Natural Gas Analyzer (NGA)], two detectors [flame ionization (FID) and thermal conductivity (TCD)], and HP 19395A Headspace Sampler (HSS). For analyses of gases in sediments.
2) Hewlett-Packard 5890A Gas Chromatograph with both FID and TCD which can accept either packed or capillary columns. For determination of low- and high-molecular-weight hydrocarbons in extracts.
3) Hewlett-Packard 3350 Laboratory Automation System (LAS). Receives data from the gas chromatographs through A/D converters and stores raw and processed data. For calibration and automated instrument runs.
4) Rock-Eval II with TOC (Total Organic Carbon) Module. For determination of source, amount, and maturity of organic matter and used primarily for petroleum monitoring.
5) Coulometrics Carbon Apparatus. For the accurate determination of inorganic and organic carbon. The Total Carbon Apparatus is used for determinations of organic carbon by difference, and a liquid sample module is available for the determination of dissolved organic carbon and total carbon in interstitial waters.
6) Carle Series 100 Analytical Gas Chromatograph. For rapid determinations of C_1, C_2, and C_{3+} in gas.
7) Perkin Elmer 240C Elemental Analyzer. For determinations of carbon, nitrogen, and sulfur in sediments.
8) Halliburton UV Fluorescence Box. For the detection of heavy hydrocarbon accumulations in the unsplit or split core. This instrument is located in the entry of the core laboratory.

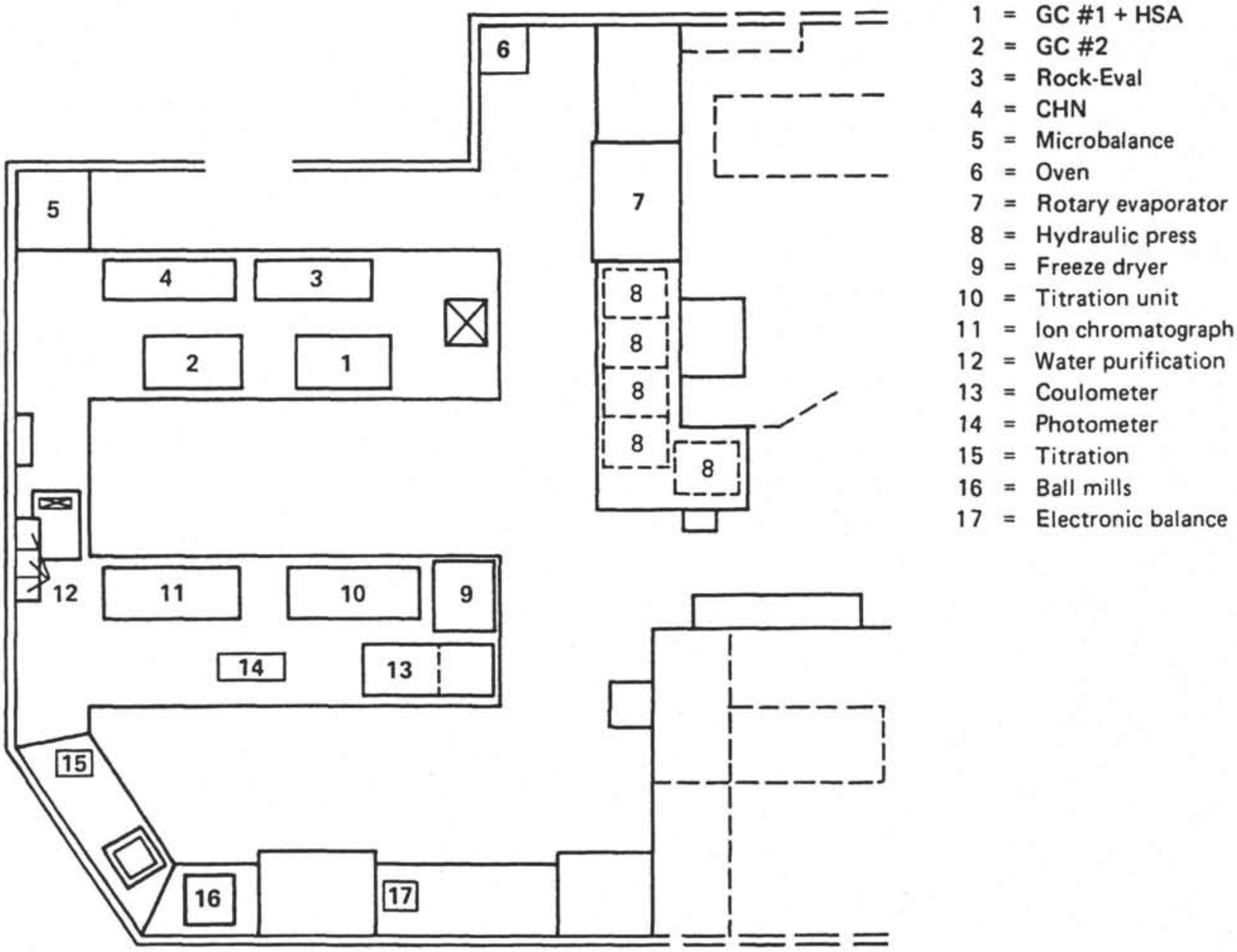


Figure 1. Floor plan of the Forecastle deck and location of instruments in the Chemistry lab.

II. GAS AND OIL MONITORING PROCEDURES

As hydrocarbon generation is a natural and inevitable result of the maturation of buried organic matter, the objective from the safety standpoint is to distinguish potentially hazardous accumulations of hydrocarbons against the background of the normal increase in hydrocarbon content with depth. For this purpose it is necessary to: (1) estimate the current capacity of the organic matter to generate hydrocarbons, and (2) compare this estimate with the actual presence of hydrocarbons, taking into account factors that could promote migration and accumulation of hydrocarbons.

The degree of organic-matter maturation and its capacity to generate hydrocarbons may be estimated by an evaluation of the following properties of gas and sediments:

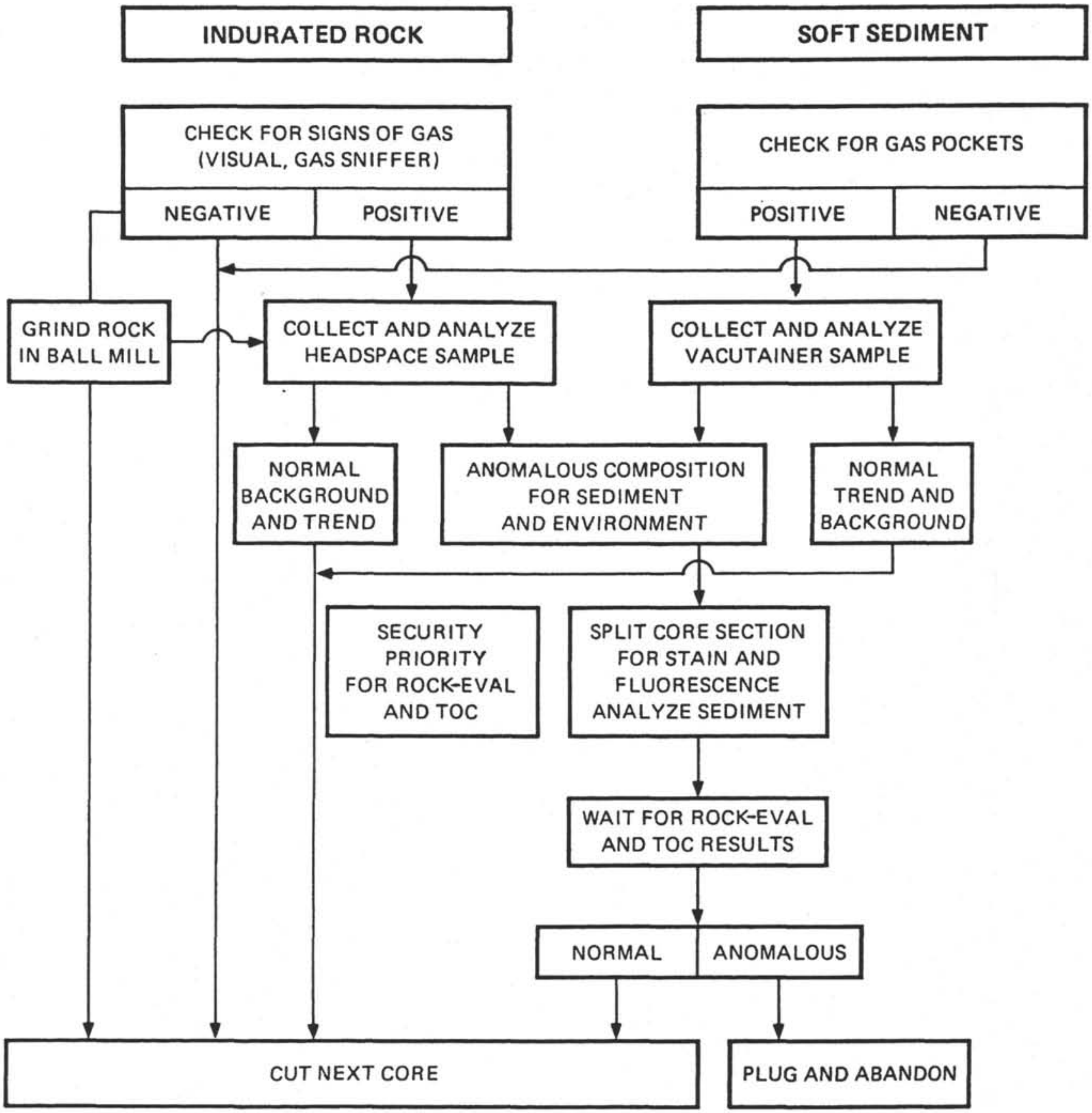
1) the content of C_2-C_5 hydrocarbons relative to methane: the C_1/C_{2+} ratio changes from more than 1,000 for immature to less than 100 for mature organic matter;
2) Rock-Eval parameters: Rock-Eval pyrolysis yields information on TOC, presence of migrated hydrocarbons, and origin and maturity of organic matter.

Evidence for the migration and accumulation of hydrocarbons may be discerned on the basis of two main features:

1) a sharp increase in the content or a change in the composition of hydrocarbons compared with that observed in overlying strata, and
2) a discrepancy between hydrocarbon content and actual maturity of the organic matter, as well as a lack of correlation between change in hydrocarbon composition and concentrations relative to lithology, stratigraphy, total-organic-carbon content, and other parameters characterizing in situ deposits.

Employing techniques outlined in Chapter III of this manual, and following routine sampling programs in the course of drilling, the geochemist can obtain information on downhole variation of hydrocarbon content and composition and can predict "normal" distribution trends of gaseous and liquid hydrocarbons. Plots of log C_1/C_2 ratios vs. depth give downhole trends, as do plots of the various Rock-Eval parameters. Deviations from these trends toward a significantly higher contribution of heavier hydrocarbons justify caution.

Figure 2 is a general flow chart of procedures and decisions to be made during real-time hydrocarbon monitoring. The decision to suspend cutting cores to wait for geochemical results may be unpopular, but in cases of "abnormal" hydrocarbon occurrences, slowing down drilling progress is much better than subjecting the ship to safety hazards and possible pollution. Details are given in the "Ocean Drilling Program Guidelines for Pollution Prevention and Safety" (JOIDES Journal Vol. XII, Special Issue No. 5, March 1986).



TIME ESTIMATES

VACUTAINER SAMPLING & ANALYSIS	C_1, C_2, C_{3+}	= 5 MINUTES
HEADSPACE SAMPLING & ANALYSIS	C_1, C_2	= 5 MINUTES
HEADSPACE SAMPLING & ANALYSIS	$C_3 - C_{6+}$	= 30 MINUTES
ROCK-EVAL SAMPLING & ANALYSIS		= 90 MINUTES
TOTAL ORGANIC CARBON SAMPLING & ANALYSIS		= 90 MINUTES

Figure 2. Generalized flow charts of analyses for hydrocarbon monitoring and of actions taken in case of hydrocarbon shows.

III. SAMPLING AND ANALYSIS

A. ROUTINE SAMPLING PROGRAM FOR SHIPBOARD ANALYSES

Sampling for the shorebased organic geochemistry studies is another important function of the shipboard organic geochemist, in addition to the main responsibility of hydrocarbon monitoring. This task provides samples for detailed organic geochemical analyses that cannot be carried out on board.

Sampling must be in compliance with the ODP Sample Distribution Policy. As is the case with any sampling routine, the collection of material for shipboard use and for shorebased research/curating must be coordinated with other participating scientists. Sample requests for all non-routine shipboard and all shorebased organic geochemistry programs are submitted to ODP on the "ODP Sample Request Form" by the individual investigators at least two months prior to the start of the cruise. These requests are approved for shipboard sampling, deferred for shorebased sampling, or rejected by the leg's Co-Chief Scientists and ODP Curator.

The shipboard organic geochemist contributes to the scientific information derived from the leg by devising a program using the shipboard facilities to obtain samples and data. The research is to be completed at shorebased laboratories following the cruise, in time for contribution to the Proceedings of the Ocean Drilling Program for that leg. The research plan is discussed with the Co-Chief Scientists prior to the leg in order to seek their agreement with the shipboard part of the program. The combination of individual research programs with the routine program on board--including results from the hydrocarbon-monitoring program--should yield optimum results in terms of sample frequency and data consistency.

1. Geochemical Parameters from Routine Sampling

Ideally, geochemical parameters measured routinely aboard ship should include the following:

- Total carbon, carbonate carbon (organic carbon by difference, except for high carbonate samples), measured with the Coulometrics CO_2 Coulometer;
- Amount of volatile hydrocarbons, amount of hydrocarbons released from thermal cracking of kerogen, temperature of maximum release of hydrocarbon from kerogen, and total organic carbon (TOC) by Rock-Eval pyrolysis;
- Composition of gas in gas pockets and in sediment by vacutainer and headspace sampling (C_1-C_{6+}, air).

In addition, shipboard facilities allow the following optional measurements:

- Dissolved organic and inorganic carbon in pore waters measured with the Total Carbon Apparatus attached to the Coulometer;
- Amount and character of extractable high-molecular-weight hydrocarbons by gas chromatography.

Inorganic geochemical measurements include:

- Concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, K^+ in pore waters by ion chromatography.

- Concentration of nitrate, ammonia, silica, and Fe^{2+} in pore waters by photometry.
- Chloride concentration, salinity, alkalinity and pH of pore waters.

To maximize the value of these analyses, they should be made on a single sample or series of adjacent samples. Time estimates for these analyses, including calibration and, in some cases, preparation, are listed in Table 1.

2. Sampling Scheme

Because many diagenetic changes occur in the topmost 100-150m of the sediment column, sampling of this interval of intense geochemical processes should be concentrated in the uppermost cores of a hole. Combining these sampling efforts and analyzing adjacent samples of gas, interstitial water, and particulate organic matter will provide an extraordinary data base for geochemical investigation and further geochemical research on shore.

Maximum information with minimum disruption of sedimentary sequences can be achieved with the following routine sampling procedure (Figure 3):

- 6 cm of whole-round sediment taken from Section 3 or 4 of Core 1 for interstitial water (5 cm) and shipboard headspace gas analyses (1 cm);
- 10-15 cm of working-half sediment taken from Core 2 for sampling of interstitial water and gas;
- 30 cm of whole-round sediment taken from Core 3 for shorebased organic geochemistry (25 cm), interstitial water (5 cm) and gas analyses;
- 10-15 cm of working-half sediment taken from Cores 4 and 5 for interstitial water and gas analyses;
- 30 cm of whole-round taken from Cores 6, 9, 12, 15, 18, etc. to total depth for shorebased organic geochemistry, interstitial water, and gas analyses.

Note: Interstitial water subsamples are stored for shorebased research; gas subsamples can be stored in vacutainers for shorebased research.

An outline of sample flow through the laboratory is depicted in Figure 4. XRD analyses and analyses other than carbonate determination on Physical Properties samples are limited by time available and priorities stated by scientists and Co-Chief Scientists. In detail, sampling and methods for individual analyses are discussed in the following paragraphs.

B. FROZEN ORGANIC GEOCHEMISTRY SAMPLES

Organic matter contained in marine sediment and rock cores is readily altered microbially and chemically through oxidation and by exposure to light. Furthermore, a vital portion of the organic matter is highly volatile and readily lost from the cores. Such alterations prior to study can result in faulty data and erroneous conclusions. Immediate shipboard study is therefore desirable, if time, manpower, and equipment permit.

When complete shipboard analyses are impossible, the best practical solution is to (1) cap, label, and promptly freeze portions of core and (2) seal selected smaller samples in labeled metal cans which are frozen

Table 1: Time estimates for routine analyses in minutes.

Analysis	Sample prep.[1]	Start up[2]	Frequency[3]	Run time[4]
Coulometer, carbonate	5	30	1/10-15	10
Coulometer, TC	5	30	1/10-15	10
Rock-Eval	5	60	1/20	20
NGA, Vacutainer	-	60	1/Site	9
GC, C_1/C_2 only	-	60	1/Site	5
GC, Headspace	5	60	1/Site	40#
GC, Headspace	10	60	1/Site	45+

1 = grinding and weighing only, drying not included.

2 = calibration, standardization, blank runs.

3 = Start-up frequency, 1/10 = blank run, calibration per 10 sample runs.

4 = Run time for one sample.

Commercial headspace analyzer, includes heating.

+ Indurated sediment.

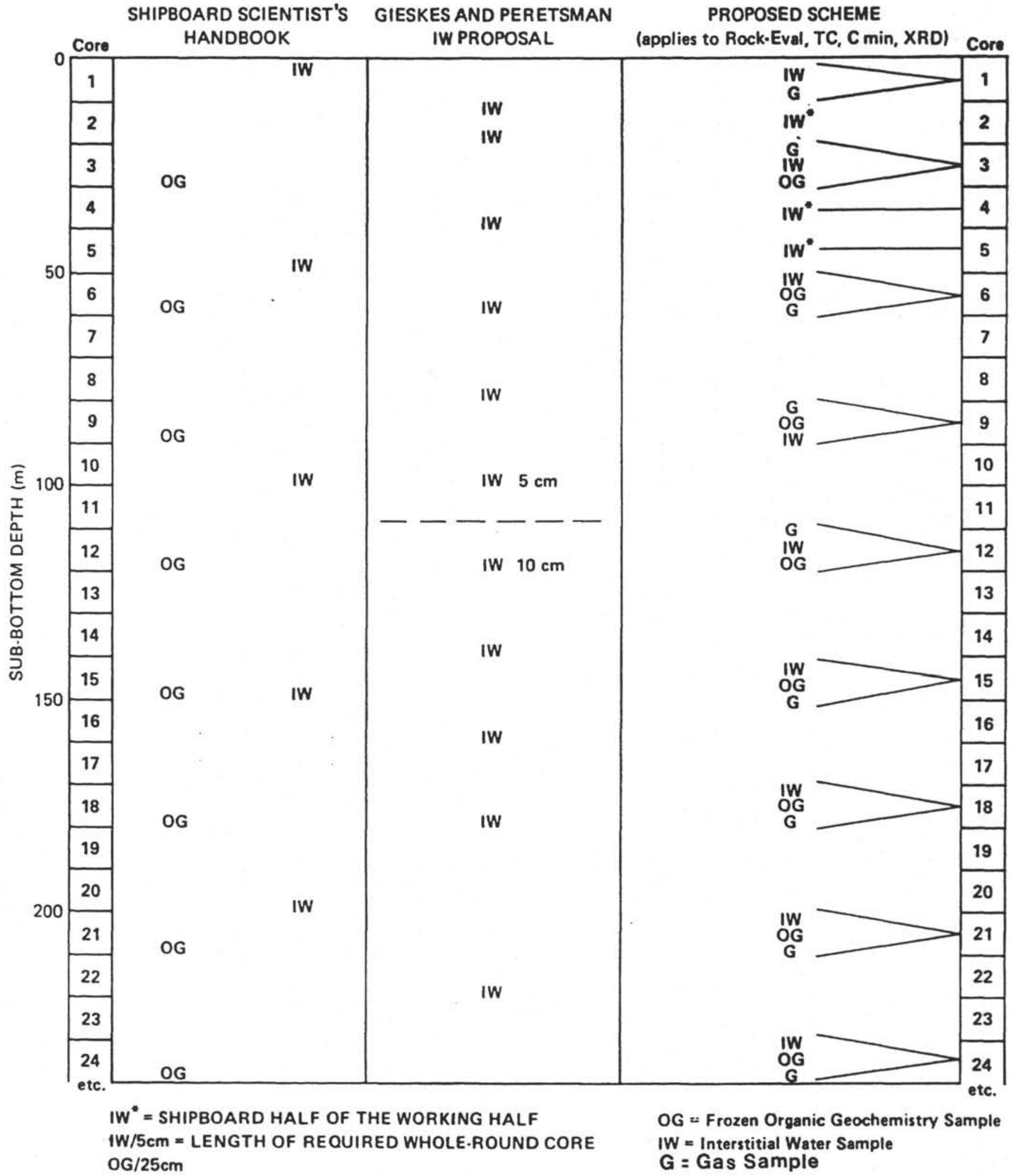


Figure 3. Sampling scheme for frozen organic geochemistry samples, gas analysis (headspace) and interstitial waters. Left column: old scheme (prior to April 1986). Center column: scheme proposed by Gieskes and Peretsman (1986) for interstitial waters. Right column: revised scheme incorporating geochemistry, gas analysis, and interstitial waters.

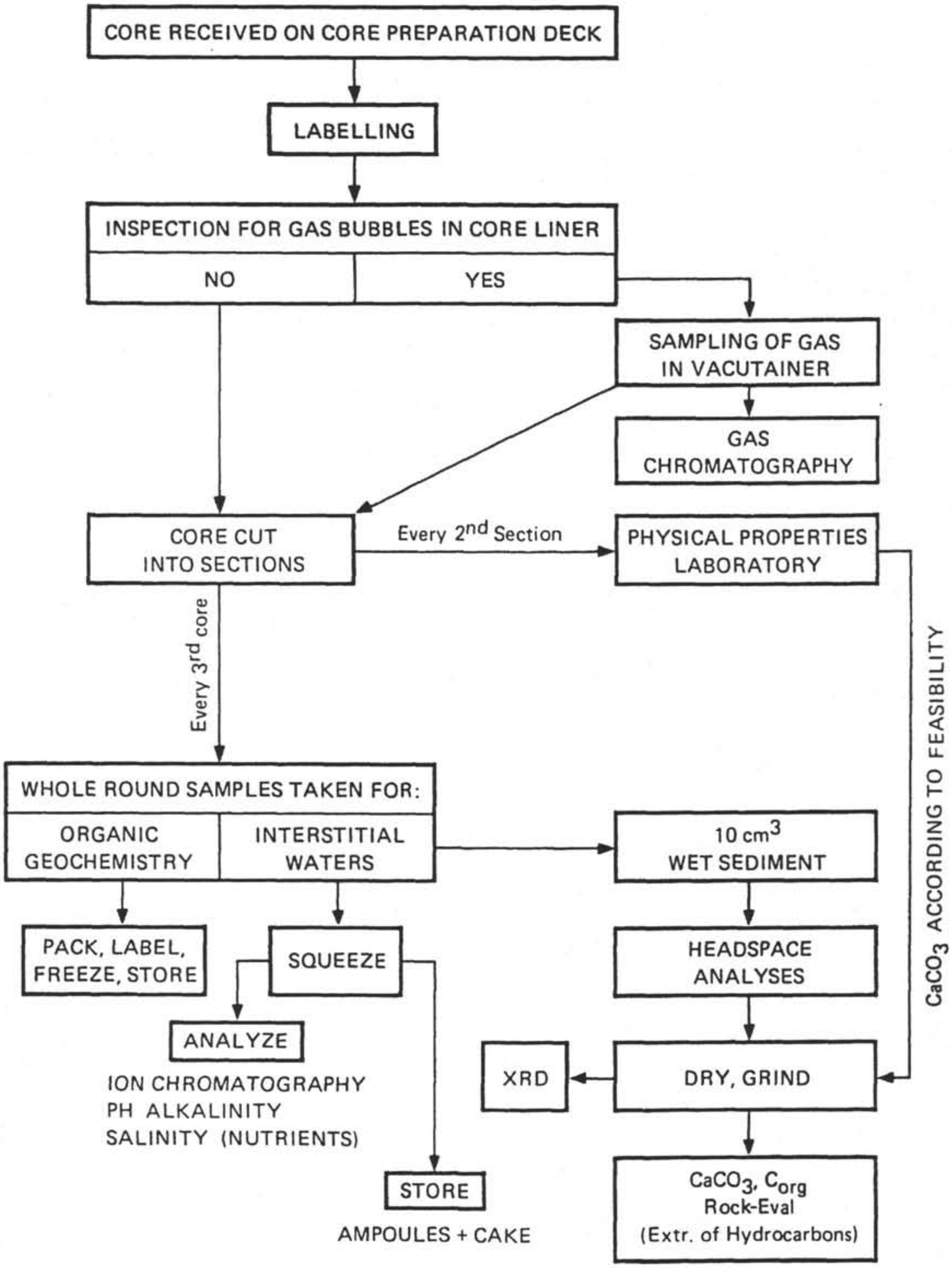


Figure 4. Generalized sample flow chart for Physical Properties and Chemistry labs.

immediately. All such samples must be maintained frozen on board, and off-loaded only after arrangements have been made for shipment of the samples in the frozen state to the ODP frozen-sample repository or directly to the requesting investigator. ODP curatorial and logistics representatives are responsible for assuring that samples are maintained in a frozen state on board ship and during transit to their destination.

Organic geochemistry (OG) samples are usually taken at each site by the chemistry technicians, assisted by the organic geochemist. This operation involves the following: 25-cm sections of sediment core may be removed every 30 meters, minimizing chances of contamination during handling. Sampling in material of high interest to the organic geochemistry community (e.g., black shales) may be increased to one section every two cores, if good recovery is achieved and at the discretion and approval of the Co-Chief Scientists and the ODP Curatorial Representative. The samples are immediately frozen aboard ship. Because these samples are frozen, they constitute a unique collection which will be available to future investigators. One quarter of every such core sample, split longitudinally, remains in permanent frozen archive. Although taking whole-round core samples interrupts stratigraphic control of the sedimentary sequence, vital information on the nature and age of significant boundary horizons is not permanently lost. It is necessary in any case to cooperate with sedimentologists and paleontologists during sampling, and sampling should be reasonably flexible.

C. ROUTINE ANALYSES FOR ORGANIC GEOCHEMISTRY

1. Gas Analysis

Besides being crucial for real-time safety monitoring of hydrocarbons, results of the routine gas-analysis procedure are of considerable scientific value. Gaseous hydrocarbons and CO_2 are, in addition to kerogen and DOC, the end-members of thermal and microbial diagenesis and catagenesis of organic matter. Interrelation of dissolved species (nutrients, alkalinity, DOC), the solid phases, and gas is complex. It is desirable to monitor all three phases downhole and, in order to maximize results, perform parallel analyses on the same sample for each of these parameters. The data base thus created is essential for further studies on the transformation of organic matter during burial.

The main objective of the shipboard gas program, however, is to assess potential safety or pollution hazards when encountering hydrocarbon accumulations during drilling.

Three methods are employed currently aboard JOIDES Resolution to sample gas and to monitor concentrations and ratios of hydrocarbon gases:

- vacutainer sampling of gas pockets in soft sediments;
- headspace techniques for gas analysis in connection with the Natural Gas Analyzer;
- rapid headspace sampling of gas in a modified ball mill for indurated sediments.

While the first and last methods are primarily intended to serve as guidelines for quick decisions concerning ship safety and pollution control, the second method produces data trends to be used (in connection with vacutainer results) for safety purposes.

a. Vacutainer Sampling

Sampling for the presence of hydrocarbon gases must be performed at all sites where there is a chance of encountering significant levels of hydrocarbons. As the core barrel is brought on deck and the core liner removed, a chemist or marine technician checks for gas pockets, bubbles, or frothing within the liner. Any evidence for abnormal hydrocarbon quantity is immediately reported to the ODP Operations Superintendent. The need to monitor for such hydrocarbons is necessary for all sediments. Generally the geochemist and technicians share the sampling and analytical work.

The organic geochemist is notified if hydrocarbons are suspected, so that samples can be analyzed immediately. Ideally, samples for gas chromatographic analysis are taken prior to cutting and capping to prevent contamination from glues and other materials used in these processes. However, the presence of gas is also marked by a bulging of the end caps of sealed core liners. As the sediments degas with the change in pressure and temperature, sections of core material are pushed apart by gas expansion. The geochemist or the chemistry technician uses a liner penetrator with syringe attachment and evacuated glass container (vacutainer) to sample these gas pockets. The sample is taken to the chemistry lab and analyzed by gas chromatography. Currently, a 5-mL sample of gas is injected into a 0.25-mL sample loop of the Hach gas chromatograph. Concentrations of components in the gas mixture are calculated from comparison with standards based on integrator results. Volume ratios of C_1/C_{2+} are plotted on log scales to observe trends in gas composition with depth. Typical trends are shown in Figure 5, a compilation of vacutainer gas composition encountered in DSDP legs.

b. Headspace analysis from unconsolidated sediments

At the time of writing this manuscript (after ODP Leg 107), the following headspace procedure was used:

Hydrocarbon gases, C_1 through C_5, were monitored on the Hewlett-Packard (HP) 5890A Gas Chromatograph plus NGA using a flame ionization detector and the HP Headspace Sampler (HSS). Methane levels were low, allowing good separation between methane and the other higher molecular-weight gases on a DC200 packed column. Run time for the analysis was 9 minutes. Methane, ethane, propane, i-butane, n-butane, i-pentane, and n-pentane are separated in order of increasing retention time and by molecular sieves. Peak areas were measured and calibrated on the HP 3392A Integrator and the HP 3350 Laboratory Automation System.

A 10-cm^3 sediment sample was collected upon initial sectioning of the core for headspace analysis. The sediment sample was placed in a 20cc glass vial and sealed immediately with a septum and crimped metal cap. The vial was then heated in a hot oil bath at 70° C for 30 minutes. The oil bath is part of the HSS. After equilibration, the HSS performs a preprogrammed sequence using an automated valve and loop sampling system. A sampling needle pierces the septum and helium pressurizes the headspace

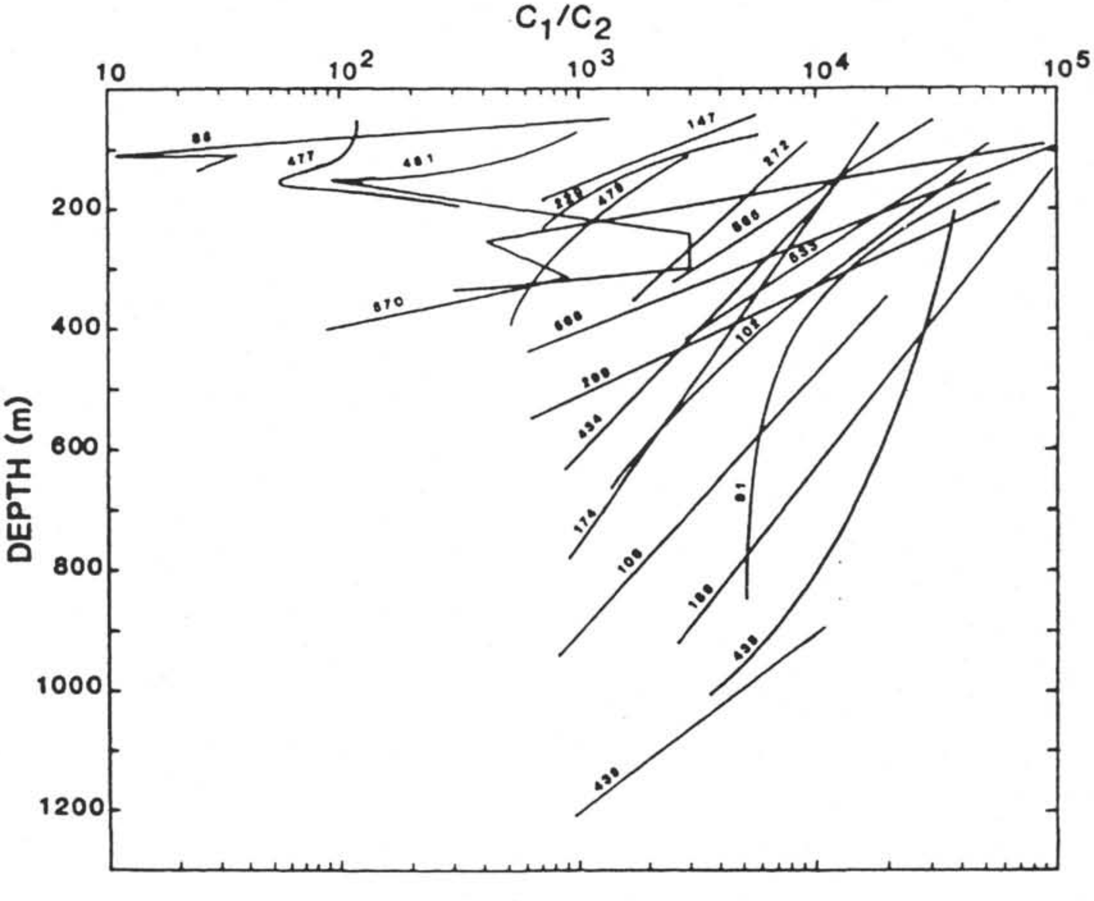


Figure 5. Variations of methane/ethane ratios in vacutainer samples from DSDP sites (Ocean Drilling Program Guidelines for Pollution Prevention and Safety. JOIDES Journal Vol. XII, Special Issue No. 5).

vial. The headspace gas passes through a 0.25-mL sample loop. The loop is then flushed into the helium carrier gas flow and the sample is delivered through a heated transfer line directly into the GC's injection port.

Concentrations of hydrocarbon gases were computed from standard sample detector responses and preprogrammed methods in the LAS system. Volume ratios of C_1/C_2 or C_1/C_{2+} are plotted on log scale to observe trends in gas composition downhole. Figure 6 compares vacutainer results with those obtained by the headspace technique on Leg 107.

c. Headspace sampling of gas from indurated sediments

Because gas evolving in indurated sediments does not form bubbles, but rather bleeds off or hisses, a rapid headspace technique designed for indurated sediments is used in conjunction with drilling operations. An approximately 5-cm^3 piece of indurated sediment is ground in a modified ball mill equipped with a septum. Five mL of gas extracted through the septum are injected into the GC sample port. Results are recorded in the same way as for the vacutainer technique.

Because of possible future changes in equipment and in sampling policy, sample spacing and preparation/analysis techniques are subject to change. We urge the organic geochemists to perform parallel analyses with vacutainers and headspace techniques wherever possible. This serves two purposes: the results of the two methods can be compared, and a data base is created for the relatively new headspace technique. Because of the small quantity of sample needed for the HSS and the NGA, we suggest that samples for HSS be taken at a rate of 1 per 3 cores, adjacent to the OG sample. After gas analysis, the headspace sample can be used for other analyses (organic-carbon determinations, Rock-Eval pyrolysis, etc.).

2. Organic Carbon

The amount of organic carbon (C_{org}) in a sample is determined in two independent ways in the chemistry lab: (1) by difference from total carbon (TC) and carbonate carbon (C_{min}) as measured with the Coulometer, and (2) by total-organic-carbon (TOC) determinations from Rock-Eval pyrolysis. At moderate-to-high C_{org} values (>0.5 wt%), and in low-to-moderate (<50%) carbonate samples, values from the two methods should agree reasonably well. At low C_{org} values, TOC readings of the Rock-Eval appear to be erratic. For samples with high $CaCO_3$ contents, the method used to compute C_{org} by difference sometimes yields negative values. Where carbonate carbon (C_{min}) is very large, the sample should be acidified, washed, and C_{org} determined directly on the residues. A comparison of methods is currently under way (Summer 1986), and the best method will be recommended for future use in the shipboard laboratory.

If not requested otherwise, TOC and source/maturity determinations by Rock-Eval follow the routine sample spacings listed in Figure 3 and are integrated in the routine program outlined in Figure 4. This sample spacing is the standard prescribed for every sedimentary hole. Additional measurements of $CaCO_3$ and TOC can be made by request from the geochemists

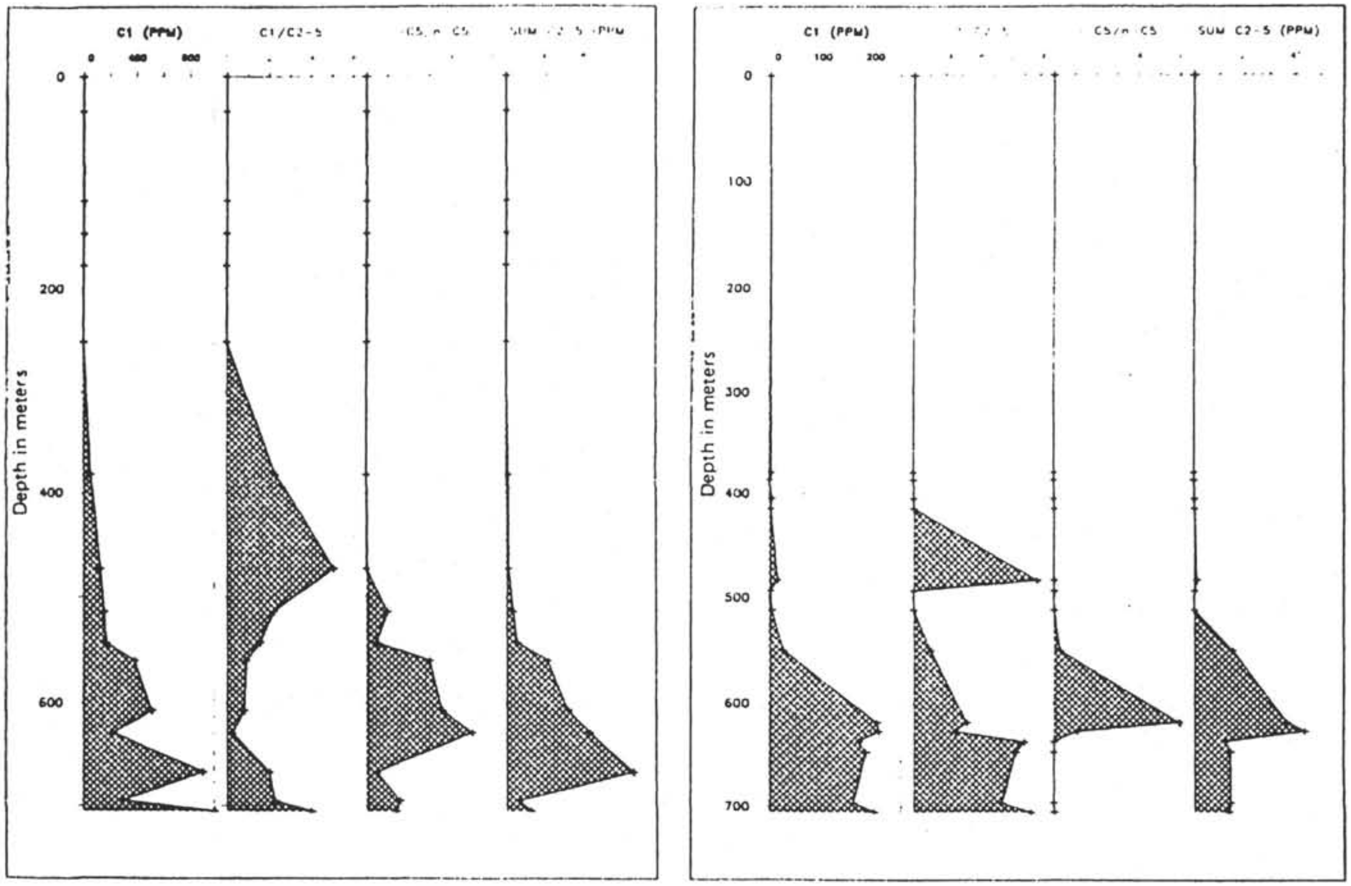


Figure 6. Comparison of results from vacutainer sampling of gas pockets (left) and headspace sampling (right) after heating 10 cm^3 of sediment in an oil bath (70^{o}C for 45 min). Samples of Site 652, ODP Leg 107.

and the rest of the scientific party if time permits.

3. Pyrolysis by Rock-Eval

Rock-Eval pyrolysis is closely associated with safety hydrocarbon monitoring because it produces values for two important sediment parameters: the amount of free hydrocarbon in the sediment (S_1) from *in situ* production and/or migration (oil/gas shows), and the amount of organic carbon present in the sample. Routinely, Rock-Eval pyrolysis is carried out on subsamples of sediment taken for interstitial water and/or gas analyses. Normally a Rock-Eval analysis is made on a sample from every third core downhole. Standard sample size is 100 mg of dried and ground sediment.

This routine sampling and analytical scheme is not used when gas-monitoring results suggest accumulations of migrated hydrocarbons in the sediments. In this case Rock-Eval analyses are done more often as needed for safety monitoring, as outlined in Chapter IV.

The Rock-Eval pyrolysis instrument was developed to serve as an exploration and screening tool for the oil industry, and the accuracy of individual measurements is sometimes debatable. Results of Rock-Eval pyrolysis are usually consistent within themselves, but when used for drawing scientific conclusions, they should be interpreted with caution. Some brief notes on interpretation and pitfalls of the method are given below.

4. Routine High-Molecular-Weight-Hydrocarbon Extraction

Extraction and analysis of high-molecular-weight-hydrocarbon compounds from sediments aboard *JOIDES Resolution* are scientific procedures which are performed in the chemistry laboratory at the request of, or by, shipboard organic geochemists. Because methodology and the experimental setup for this kind of analysis are not standardized throughout the scientific community, it is reasonable to assume that scientists intending to perform extraction and analysis in the shipboard laboratory will have their own methods. We suggest using the procedure outlined below on board when information on the high-molecular-weight hydrocarbons is needed for safety monitoring. Although the procedure is rather simplistic, results will be comparable within the scientific framework of ODP. Elaborate characterization of extractable organic matter will still be restricted to shorebased research, because manpower, laboratory space, and instrumentation needed will commonly not be available during cruises.

On Leg 107 the following procedure was employed and yielded good results: Selected samples were subjected to solvent extraction in order to tentatively characterize origin and maturity of organic matter. About 20 grams of each sample were freeze dried, ground, weighed, and ultrasonicated for 2 hours with a mixture of methanol/toluene (3:1). After centrifuging and decanting the solution of extractable hydrocarbons, the extract was evaporated to dryness in a rotary evaporator and weighed. In most cases, the small amount of sample and of the resulting extract precluded quantification. The dried extract was redissolved in HPLC-grade n-hexane, and saturated hydrocarbons were separated from aromatic and NSO components by liquid chromatography on commercial CN and silica gel columns (Baker 10, provided in the laboratory). The hexane eluent from these columns was again evaporated and redissolved in 1 mL of hexane. Two microliters of this hexane solution were injected into the HP 5890A gas chromatograph equipped with a 25-m high-performance capillary column. Instrument setup and column characteristics are given in Table 2.

Retention times from an n-alkane standard were used to identify saturated compounds. Results were reported through the HP Laboratory Automation System and plotted with the CPLOT routine. Ratios of components were computed after manual background correction and automated integration of peaks.

Table 2: Experimental conditions for gas chromatography.

Instrument	Hewlett Packard 5890A
Temperature program	Injection at 200°C, detector (FID) 300°C, initial temperature (1 min) 40°C, rate A 50°C/min to 80°C, purge on after 0.8 min, 1 min at 80°C, rate B 10°C/min to 300°C, 300°C for 5 min.
Column	25-m HP Ultraperformance capillary, cross-linked methyl silicone, internal diameter 0.2mm, film thickness 0.11 micron, splitless injection
Run time	30 min

IV. DATA INTERPRETATION: A BRIEF GUIDE

The responsibility for integrated interpretation of the multidisciplinary data from hydrocarbon monitoring rests with the Co-Chief Scientists in consultation with the ODP Operations Superintendent. They decide whether drilling continues or the hole is plugged and abandoned. Nevertheless, the shipboard organic geochemist should devise his own forecast and make it known to the Co-Chief Scientists and the Operations Superintendent. He should be prepared to explain the scientific rationale by which the conclusions were reached.

The following is a suggested stepwise procedure for developing a continuing forecast with regard to the potential of encountering an accumulation of petroleum as drilling in a hole proceeds. Minimizing time for sample collection and analysis is essential. Data and conclusions must be developed immediately to be of value for safety considerations.

There are three basic types of potentially hazardous petroleum occurrences:

1) Migrated petroleum: petroleum, consisting of natural gas and/or crude oil, generated in fine-grained rocks derived from argillaceous or lime muds, which subsequently migrated into adjacent coarser grained, more permeable rocks or clastic sediments;

2) Petroleum from anomalous thermal regimes: petroleum generated in rock units which have been exposed to thermal regimes considerably higher than those near the water/sediment interface, and which has migrated to geological reservoirs; and

3) Gas hydrates: natural gas accumulated as gas hydrate at relatively shallow depth, which may be acting as a cap or seal for gas and possibly for crude oil.

A. GAS GEOCHEMISTRY

Methane is ubiquitous in all organic-rich, fine-grained sediments. Ethane and higher hydrocarbons are usually generated slowly with depth. Increasing proportions of ethane and the higher homologs relative to methane with depth are normal results of increasing thermal maturation of organic matter. For petroleum accumulations of different types, the indicators which might show an approaching hazardous situation can vary widely. Ethane and higher hydrocarbons are generated at shallow depths. Neopentane (2,2-dimethyl-propane) often is present in these hydrocarbon mixtures in larger concentrations than ordinarily occurs in older, more mature mixtures. Accordingly, a progressive decrease in the ratios of methane to ethane, methane to propane, etc., indicates either (1) advancing stages of thermal genesis, and hence an increasing potential for petroleum to accumulate in adjacent porous strata from which it could be suddenly released, or (2) an approach to an accumulation of mature petroleum which has migrated from depth. As a general guideline, values less than those indicated below for composition of gas in gas bubbles (vacutainers) justify caution:

methane/ethane	200
methane/propane	2000
methane/n-butane	15,000.

The values above must not be used without qualifying considerations. For example, a significant concentration of neopentane (i.e., concentrations of more than about 10 ppm) suggests that petroleum genesis is in a very early stage, and an accumulation of petroleum in sufficient concentration to cause a hazardous release is unlikely. A thin underlying sedimentary section, that is, a thin interval to basement, would support the conclusion of low risk.

A rapid increase in the concentrations of the individual light hydrocarbons followed by a sharp decrease should be viewed as a possible hazardous situation, particularly if the drill is approaching an underlying interval where increased porosity (e.g., sand) is expected. In this case the rapid rise in hydrocarbon concentrations might suggest penetration of a thick, low-permeability, overpressured source rock. As the boundary of the more porous and permeable underlying unit is approached, decreased hydrocarbon concentrations in the local rock, and flushing of hydrocarbons into the adjacent unit may have occurred, with petroleum finally collecting in structural highs. On penetration of the underlying high-porosity unit by the drill, collected gas accumulations may be readily released.

Large ratios of methane to higher hydrocarbons do not necessarily indicate that drilling ahead is without hazard. For example, gas percolating upward from the leading edge of a gas-hydrate accumulation may be low in ethane plus higher hydrocarbons. The hazard does not lie in the gas-hydrate zone but in the sediments immediately below, where gas and perhaps petroleum may be pooled beneath the gas-hydrate seal.

Methane with little associated higher hydrocarbons is commonly generated from the microbial decomposition of organic material at depth. Potential sources of gas can be evaluated from microscopic kerogen characterization by the shipboard palynologist/paleontologist. If, for example, the rock (1) contains large amounts of terrestrially derived macerals (vitrinite), (2) displays high vitrinite reflectance measured in polished blocks, (3) shows dark color of organic debris (TAI: Thermal Alteration Index; Figure 7), and (4) has high thermal maturity as determined from pyrolysis parameters, we would expect increasing amounts of thermally derived methane. In such a situation, particularly on approaching a seismic reflector, utmost caution is advised and continuous gas monitoring is essential because of the potential hazard. Many parameters needed to determine diagenetic zones of organic matter (OM) maturation (Figure 7) can be analyzed on board ship. Appendix C is a reprint of a summary article on gaseous hydrocarbons in marine sediments.

B. GAS HYDRATES

The presence of gas hydrate is often indicated by an anomalous seismic reflection event (BSR: Bottom Simulating Reflector) that approximately parallels the bathymetry and occurs at sediment depths predicted from the pressure-temperature stability field for gas hydrates (Appendix D). The Co-Chief Scientists and the ODP Operations Superintendent should be aware of the location of possible gas-hydrate accumulations, and, currently, approval by the JOIDES Pollution Prevention and Safety Panel is required before suspected gas hydrates can be sampled. When gas hydrates are

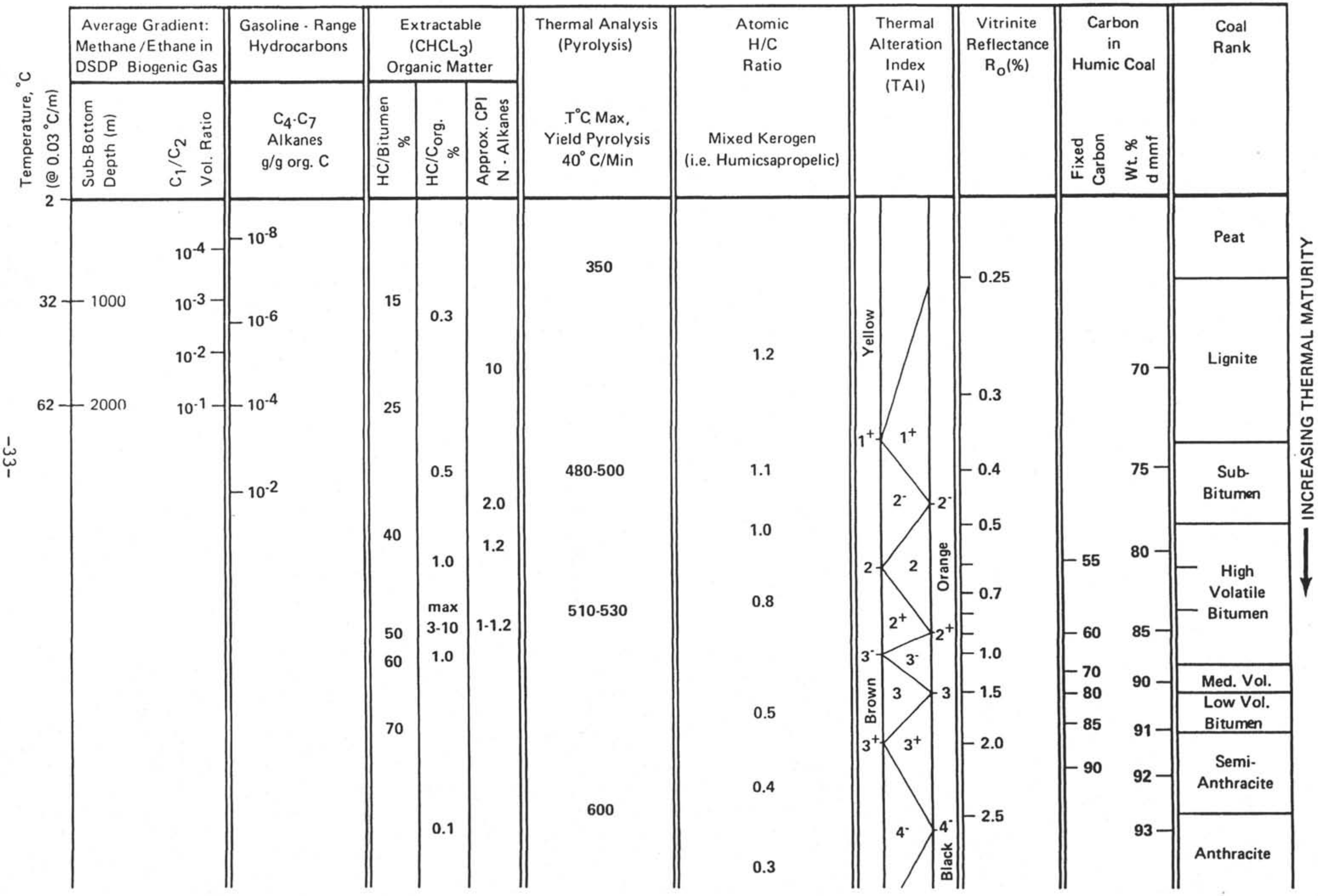


Figure 7. Simplified chart to compare various indicators of thermal maturity in sediments.

drilled, caution and very close monitoring by the organic geochemist is required. The greatest danger lies in a gas and possible oil accumulation immediately below the gas-hydrate layer. Where gas hydrates have been recognized, previous drilling has always terminated at least 100 meters above the base of the suspected gas hydrate. If solid material is recovered that is thought to contain gas hydrates, verification can be obtained by placing a piece of recovered core material into a carbonate bomb or similar device. Gas hydrates are likely present if the volume of gas evolved exceeds that of sediment by a factor of about 3 or more.

C. BITUMEN GEOCHEMISTRY

Examination of cores for hydrocarbon fluorescence under ultraviolet light often indicates oil in small amounts, or oil of light color that might not be detected by other means. Oil-stained samples that are old may not fluoresce; thus, failure to fluoresce should not be taken as decisive evidence of absence of hydrocarbons. If hydrocarbons are suspected, cores should be split upon arrival on deck and be inspected under UV excitation in the Halliburton UV box located in the entry to the Core Laboratory. Yellow to brown fluorescence indicates bitumen accumulation. All samples suspected of containing hydrocarbons should be extracted with petroleum ether or methanol/toluene (3:1) and examined by UV fluorometry. Further examination by pyrolysis is essential, and additional investigation by gas chromatography may be warranted.

The following is a method of testing for hydrocarbons employed in commercial drilling. It is fast and can easily be performed on the ship while data are being collected from pyrolysis. To test cores, a few grams of dried sediment are placed in a white porcelain evaporating dish and covered with reagent. It is important that the sediment be dried thoroughly at low temperature, otherwise water within the sample may prevent penetration by the solvent, thus obscuring decisive results. The hydrocarbon extracted by the solvent is called a "cut." The cut is observed under normal light and should be described on the basis of the shade of the coloration, which will range from dark brown to no visible tint.

The most reliable test for hydrocarbons is the "<u>cut fluorescence</u>" test. In this test the effect of the solvent on the sample is observed under ultraviolet light, along with a sample of the pure solvent as control. If hydrocarbons are present, fluorescent "streamers" will be emitted from the sample, and the test is evaluated by the intensity and color of these streamers. Some shows will not give a noticeable streaming effect but will leave a fluorescent ring or residue in the dish after the reagent has evaporated. This effect is termed a "residual cut." Generally, low-gravity oils will not fluoresce but will cut a very dark brown, and their "cut fluorescence" may range from milky white to dark orange. If no fluorescence is exhibited by the core-catcher samples or their solvent extracts, it can be assumed that liquid petroleum is not present. A dull, yellow-brown fluorescence indicates an asphaltic residue and in itself does not indicate a drilling hazard. Yellow, green, and blue fluorescence indicates asphaltic oil, light oil, and naphtha or gas condensate, respectively. The hazard to safety increases in that order.

With sophisticated shipboard instrumentation and capabilities to perform gas chromatography on extracts, further qualitative and quantitative analyses of high-molecular-weight hydrocarbons in extracts can be performed rapidly and easily, but sometimes results suffer from contamination of samples from shipboard contaminants. Certain shipboard oils and greases such as pipe dope, cable grease, and core barrel lubricant can get into the core catcher, and even occasionally inside the core liner. A catalogue of geochemical fingerprints for possible contaminants has been prepared as ODP Technical Note #6. This note contains gas chromatograms of solvent extractable hydrocarbons in potential organic contaminants. If contamination is suspected, a sample or samples of sediment should be obtained from a freshly cut core section. No safety alarm should be issued until contamination has been ruled out. A rapid gas-chromatographic analysis, including sample preparation, can be performed within 30 minutes.

D. ORGANIC-CARBON GEOCHEMISTRY

Biological synthesis of reduced (from CO_2) carbon compounds is the source of organic carbon in sediments underlying the world oceans. Depending on light penetration and nutrient supply, annual primary production of organic carbon (49×10^9 ta^{-1}) varies greatly from shelf areas and areas of upwelling (about 100 g C $m^{-2}a^{-1}$ and 300 g C $m^{-2}a^{-1}$, respectively) to open-ocean waters of low productivity (about 50 g C $m^{-2}a^{-1}$).

Of this organic carbon produced in the euphotic zone of the water column, only about 0.1% finally is preserved in sediments. The remaining 99.9% is oxidized during sinking or during benthic consumption. Even in anoxic sediments of high sedimentation rates underlying oxygen-deficient water bodies (settings ideal for preservation of organic matter) the percentage of primary-produced carbon finally preserved hardly exceeds 5%. Nevertheless, sedimentary rocks (of all ages) make up the largest reservoir of organic carbon on Earth, estimated to contain about 10^{22} g of reduced carbon. Average values for open-marine sediments are about 0.1% by weight; potential oil and gas source rocks are defined to contain more than 0.5% (detrital rocks) and 0.3% (carbonate and chemical rocks).

Observations on the interrelation of sedimentation rate, primary production, and preservation of organic carbon in sediments permit an estimate of ancient primary productivity for any given sedimentary unit. Accumulation rates of organic carbon can be computed by data obtained aboard ship:

$$Ac_{org}[g/cm^2/1000yr] = C_{org}\ [\%] \times \frac{WD - (1.025 \times P)}{100} \times S$$

where
WD = wet bulk density of sediment;
1.025 = density of pore water;
P = porosity;
S = sedimentation rate [cm/1000yr].

Paleo productivity can be reconstructed, employing an empiric relationship derived from various sedimentary environments:

$$R = \frac{C \times DD\,(1-P)}{(0.003)\,S^{0.3}}$$

where R = paleo productivity [$g/m^2/yr$];
C = C_{org} [wt. %];
DD = dry density = wet density - [1.025 X P];
P = porosity;
S = linear sedimentation rate [cm/1000yr].

Contributions to organic matter are derived from different sources:

- Marine phytoplankton;
- Phytobenthos in shallow water with sufficient light;
- Bacteria;
- Allochthonous, land-derived organic material.

These sources can be identified by various methods, of which Rock-Eval pyrolysis, petrographic investigation of kerogen, and gas chromatography of solvent extracts can be performed aboard ship.

Factors that help preserve organic matter in quantities above the 0.1% "background" level are:

- Oxygen depletion in bottom waters or in sediment as a result of high organic input;
- Adsorption of certain compounds to mineral particles;
- Preservation of organic compounds as shell constituents;
- Changes in the rate of deposition of sediment organic matter, disrupting the steady state of input and benthic consumption;
- High input of terrigenous organic compounds which are more stable than marine organic matter;
- Dominant input of argillaceous sediments where oxygenation of pore water is restricted.

The background organic carbon in open marine sediments is partially composed of recycled, highly oxidized material of continental origin (the petrographic term is inertinite) and amorphous, uncharacterized remains (probably of bacterial origin).

Organic matter undergoes changes in composition similar to changes in mineral assemblages with increasing burial depth. The three consecutive steps in organic matter transformation are termed diagenesis, catagenesis, and metagenesis. Boundary conditions for this sequence are given mainly by temperature and burial time; pressure contributes only insignificantly. Arbitrary boundaries can be determined by vitrinite reflectance. The general scheme of evolution of the organic fraction and the hydrocarbons produced are depicted in Figure 8.

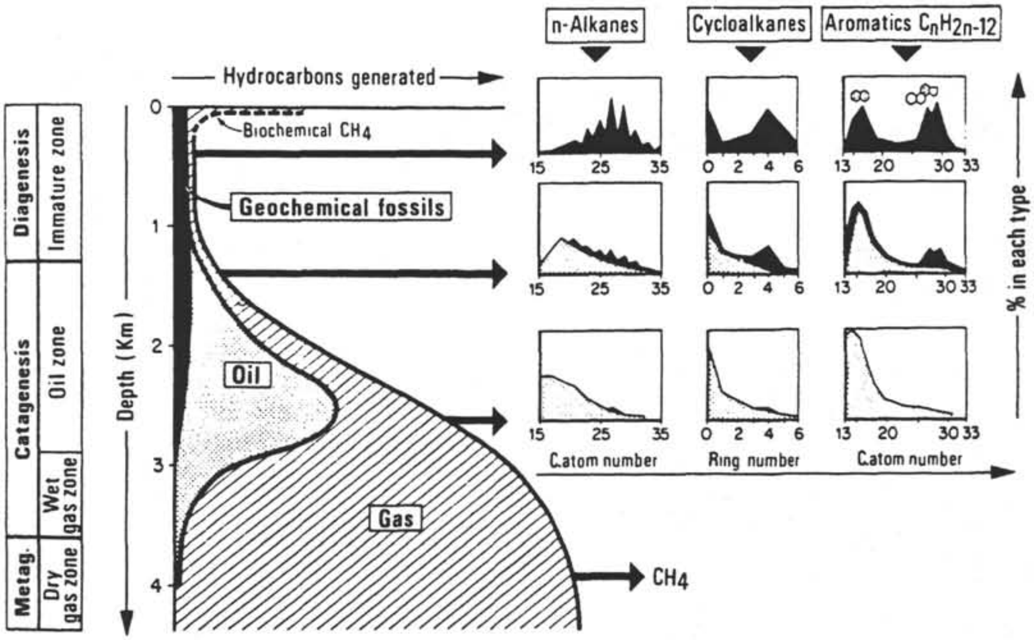


Figure 8. General scheme of hydrocarbon formation as a function of burial of source rocks. Actual depths vary according to particular geological situation and heat flow. (From: B.P. Tissot & D.H. Welte, 1984. Petroleum Formation and Occurrence. Springer, Berlin, Heidelberg, New York, Tokyo, 2nd edition.)

E. PYROLYSIS

The organic geochemist and chemistry technicians should operate the Rock-Eval pyrolysis instrument in close coordination with drilling to obtain significant data for evaluation of potential hazards. For example, Rock-Eval pyrolysis can provide preliminary information on the stage of petroleum genesis, petroleum potential and whether migration has taken place.

1. Procedure

Rock-Eval pyrolysis is used to rapidly identify the type and maturity of organic matter in whole rock samples. Samples of ground rock, about 100 mg, are pyrolyzed in a helium atmosphere at $300^{\circ}C$ for 3-4 minutes, followed by programmed pyrolysis at $25^{\circ}C/min$ to $550^{\circ}C$. Analysis time per sample is about 30 minutes including TOC determination and cooling. Automatic sampling allows for serial analyses of 24 samples. Figure 9 shows the flow schematic in the Rock-Eval, where helium is used as the carrier gas.

The S_1 and S_2 peaks are detected by the FID (Flame Ionization Detector), whereas the S_3 peak from thermal cracking of kerogen is detected by a TCD (Thermal Conductivity Detector) after entrapment of CO_2. The S_1, S_2, and S_3 peaks are determined while the sample is in the first oven (the oven on the left). The sample is heated in a temperature program to release free hydrocarbons and subsequently liberates hydrocarbons from cracking of kerogen. In the second oven the sample is oxidized in an oxygen atmosphere to give a reading for Total Organic Carbon (TOC). All of the inorganic carbon has burned off below 600° C in the first oven. The TOC is analyzed using the CO_2 trap and the TCD in the TOC module. Figure 10 shows a typical Rock-Eval trace.

2. Guide for interpretation of Rock-Eval results

The parameters resulting from Rock-Eval pyrolysis are as follows:

T_{max} ($^{\circ}C$): The temperature at which maximum release of hydrocarbons from cracking of kerogen during pyrolysis occurs (peak of S_2).

S_1 (mg hydrocarbon/g rock): The quantity of free hydrocarbons (oil and gas) present in the rock and which are volatilized below $300^{\circ}C$.

S_2 (mg hydrocarbon/rock): This peak gives the amount of hydrocarbon type compounds produced by the cracking of kerogen as the temperature increases to $550^{\circ}C$. This also shows the quantity of hydrocarbons which could be produced in this rock should burial and maturation continue.

S_3 (mg CO_2/g rock): Quantity of CO_2 produced from pyrolysis of the organic matter in the rock up to $390^{\circ}C$.

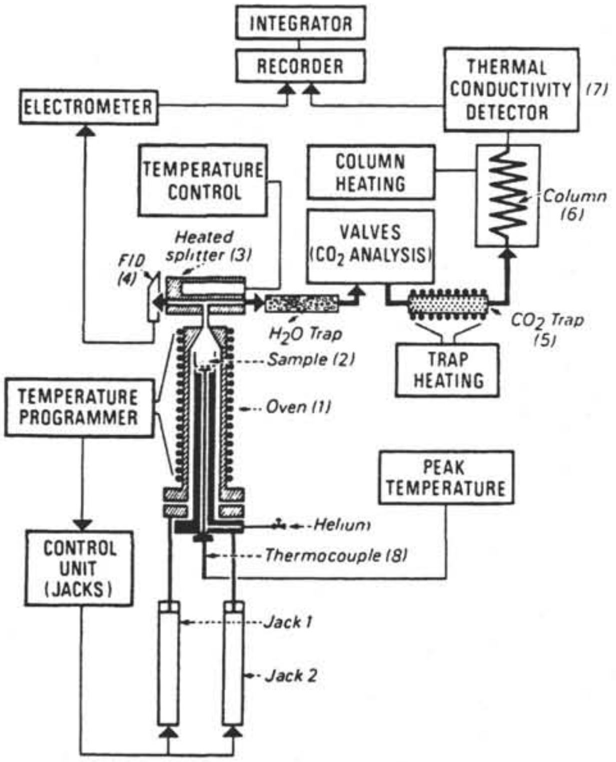


Figure 9. Schematic diagram of Rock-Eval pyrolysis device. From: Tissot & Welte (1984). Petroleum Formation and Occurrence. Springer, Berlin, Heidelberg, New York, Tokyo, 2nd edition.

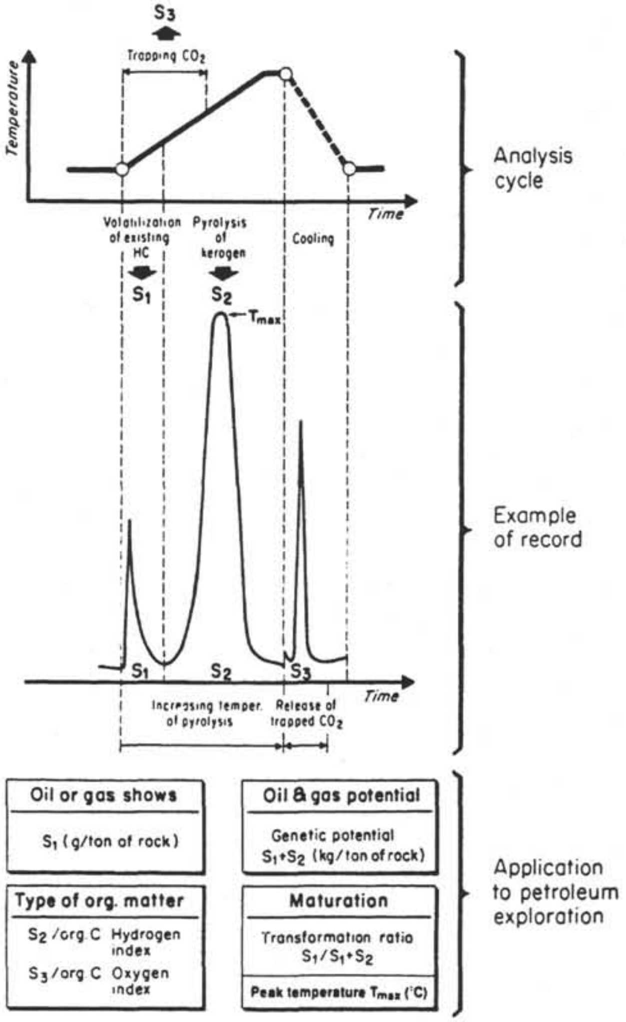


Figure 10. Example of a Rock-Eval trace. From: Tissot & Welte (1984). Petroleum Formation and Occurrence. Springer, Berlin, Heidelberg, New York, Tokyo, 2nd edition.

PRODUCTIVITY INDEX (PI): $=S_1/(S_1 + S_2)$. PI characterizes the evolution level of the organic matter ("See Oil Shows" below). PI typically increases with depth and can therefore pinpoint areas with above or below average presence of hydrocarbons.

S_2/S_3: A means of determining the type of organic matter in the rock (See "Type" below).

PETROLEUM POTENTIAL (PC): $= k\ (S_1 + S_2)$, where $k = 0.083$ mg carbon/g rock. Pyrolyzed carbon (PC) corresponds to the maximum quantity of hydrocarbons capable of being produced from the source-rock given sufficient burial depth and time.

TOTAL ORGANIC CARBON (TOC): Weight percent of organic carbon can be determined independently and entered into the program or the TOC module can determine the TOC.

HYDROGEN INDEX (HI): $= (100 \times S_2)/\mathrm{TOC}$. Is a parameter used to characterize organic matter as to its origin. Marine organisms and algae in general are composed of lipid- and protein-rich organic matter, where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants. HI typically ranges from about 100 to about 600 in geological samples.

OXYGEN INDEX (OI): $= (100 \times S_3)/\mathrm{TOC}$. Indirectly determines the ratio of O to C, which is high for polysaccharide-rich remains of land plants and inert organic material (residual organic matter) encountered as a background of C_{org} in most marine sediments. Values range from near zero to about 150. The classification of different kerogen types according to their HI/OI characteristics is depicted in Figure 11.

Using the parameters shown in Table 3, one can assess the possible type, maturation and oil shows of the rock.

TYPE: Plotting HI against OI, as in Figure 11, provides a guide to three types of organic matter.
This diagram is similar to the familiar Van Krevelen Diagram, which was atomic H/C and O/C ratios in kerogen to distinguish between different types of organic matter.

Type I: algal, oil prone (lipid- and protein- rich)
Type II: marine, oil/gas prone (intermediate)
Type III: terrestrial, gas prone (lignin-rich)

S_2/S_3: 0.0 - 2.5 = gas, Type III
2.5 - 5.0 = oil/gas, Type III
5.0 - 10.0 = oil, Types I and II

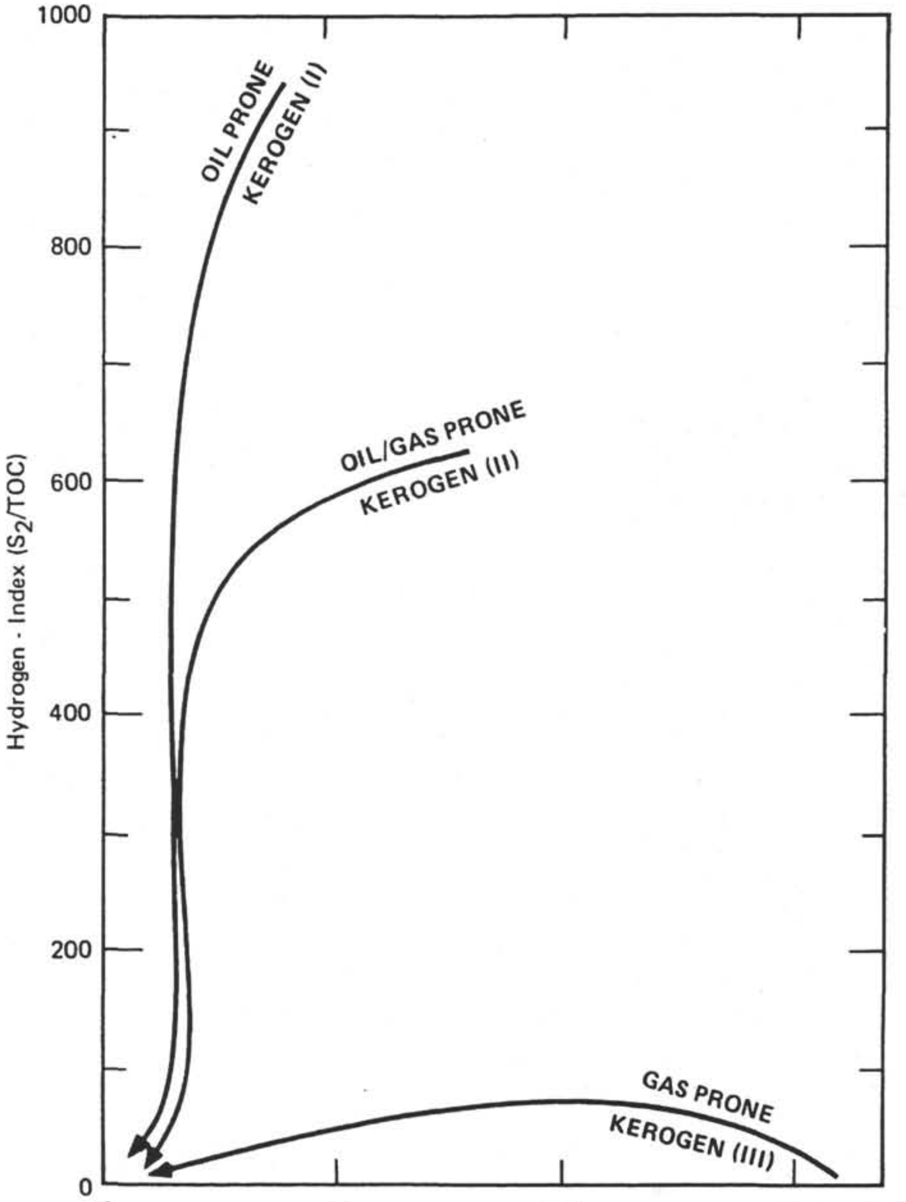


Figure 11. HI/OI plot from Rock-Eval pyrolysis data. This is an adapted version of the so-called Van Krevelen diagram, relating chemical characteristics of organic matter in sediments to origin of organic matter, maturity, and type of hydrocarbons produced.

Table 3: A sample printout of Rock-Eval parameters which are described in the text.

DEPTH	QTY (mg)	TMAX	S_1	S_2	S_3	PI	S2/S3	PC	TOC	HI	OI
1	50.1	423	3.25	45.64	1.09	0.07	41.87	4.07	11.45	398	9
2	49.6	423	3.08	45.52	1.29	0.06	35.28	4.05	11.51	395	11
3	54.3	424	3.11	45.35	1.32	0.06	34.35	4.03	7.03	645	18
4	100.0	431	0.33	9.36	0.97	0.03	9.64	0.80	1.43	654	67
5	100.1	431	0.26	9.11	1.23	0.03	7.40	0.78	1.28	711	96
6	101.4	429	0.33	9.51	1.42	0.03	6.69	0.82	1.11	856	127
7	101.5	438	4.18	88.98	3.66	0.04	24.31	7.76	11.35	783	32
8	100.5	439	3.59	87.40	3.62	0.04	24.14	7.58	8.12	1076	44
9	103.5	425	0.04	0.05	1.00	0.50	0.05	0.00	0.18	27	555
10	105.0	355	0.04	0.06	0.78	0.40	0.07	0.00	0.15	40	520

MATURATION: There are three ways to estimate maturation:

1. Location of HI and OI on diagram in Fig. 11. The arrows point towards increasing maturation.

2. According to parameter T_{max}:
   $400^{\circ}C - 430^{\circ}C$ = Immature
   $435^{\circ}C - 450^{\circ}C$ = Mature or Oil Zone
   $450^{\circ}C - 470^{\circ}C$ = Gas Zone

3. PI:
   In an ideal situation with increasing burial depth, S_1 should increase and S_2 should decrease; thus the PI will increase with depth and maturation.

OIL SHOWS: PI will increase regularly with depth (Fig. 12a) and increase rapidly in zones of hydrocarbon accumulation (Fig. 12b).

Interpretation of Rock-Eval data must be done cautiously and several pitfalls of the method need to be taken into account:

Quantity of Organic Matter (TOC)

Rock-Eval II with TOC Module yields very good data in samples of relatively low maturity (<1% R_o). Comparison with various combustion methods showed that Rock-Eval data are quite accurate (G. Claypool, pers. comm. 1985). Because of the relatively low combustion temperature, very mature organic matter may not be oxidized to CO_2, and values will be too low.

Type of Organic Matter: HI versus OI

Results should be verified by independent methods (maceral microscopy, kerogen investigation etc.). Immature sediments frequently show poor correlation between HI and atomic H/C and OI and atomic O/C. Very often, samples plotted on the HI/OI plot fall in between the general paths, or outside the range of the three major kerogen types. A fourth kerogen path below type III has been suggested by various authors in order to describe highly oxidized, residual organic material.

Thermal Maturity of Organic Matter

T_{max} and the Production Index (PI) are rough measurements of maturity only. Type of OM appears to affect the values.

Levels of thermal maturation are given by PI plus T_{max} as follows:

Immature	PI	<0.1	T_{max}	$<435^{\circ}C$
Onset of oil generation	PI	0.1	T_{max}	$435 - 445^{\circ}C$
Oil window		0.4		$445 - 470^{\circ}C$

Bitumen Content

S_1 is an independent measure of the amount of bitumen in a sample although it does not necessarily correlate to solvent-extractable bitumen.

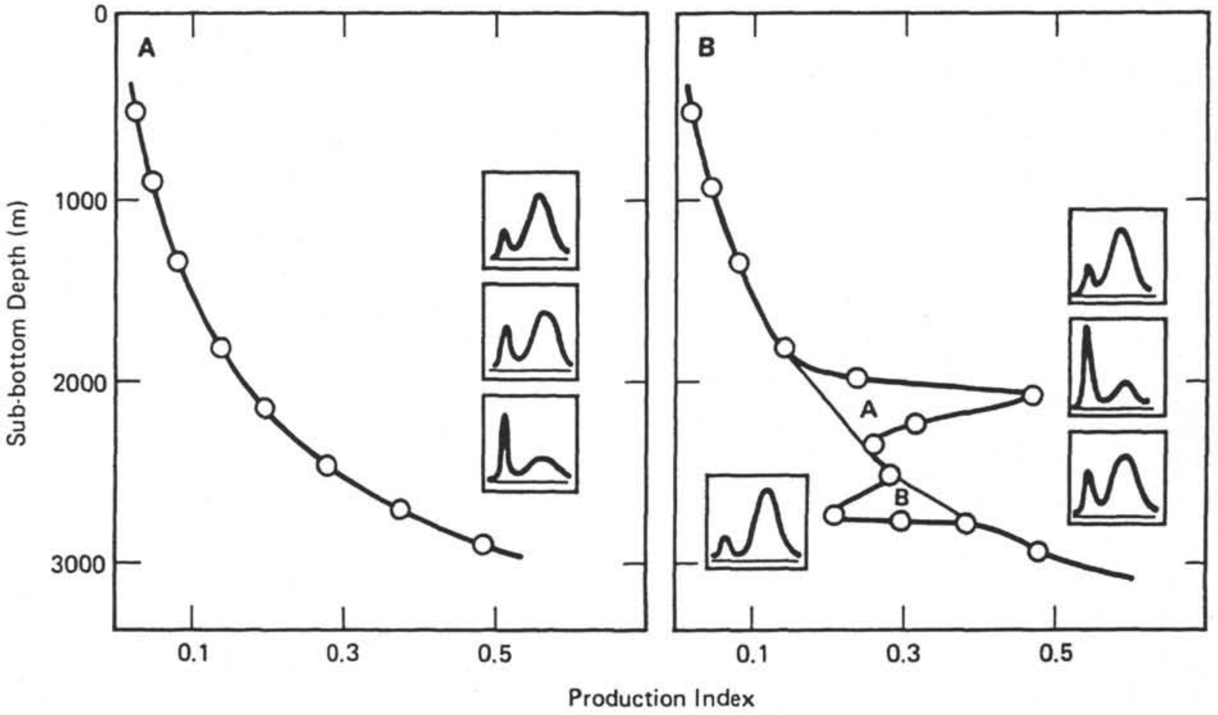


Figure 12. Productivity Index (PI) derived from Rock-Eval pyrolysis. PI increases smoothly with depth when no migrated hydrocarbons are encountered in the sediments (a). Rapidly increasing PI indicates the presence of migrated hydrocarbons (b).

Migrated oil contributes to this peak, and heavy oil and tar may influence S_2 and T_{max}.

Interference by mineral matrix of samples low in TOC

For clay-rich rocks with less than 0.5% TOC, HI values are too low and T_{max} too high because of absorbtion phenomena. This is especially true in illite-rich claystones. Sample sizes should always be the same (100mg), but even if sample sizes are the same, derived variables (S_2/TOC and S_3/TOC) may be quite erroneous.

Further literature on Rock-Eval data interpretation can be found in the citations of Appendix C.

V. ACKNOWLEDGMENTS

This manual represents an extensively revised version of the "Shipboard Organic Geochemistry Guide/Handbook" compiled in 1981 by Bernd R.T. Simoneit. Assistance in the preparation of the revision has been provided by numerous ODP Marine Technicians and staff. D. Marsee provided updates on the bibliography concerning organic geochemistry in DSDP Initial Reports.

APPENDIX A: Shipboard Geochemical Procedures

1. Instrumentation

The following paragraphs are short descriptions of main instruments available in the laboratory. For more detailed information, refer to the manuals present in the laboratory or ask the technicians onboard ship. Instrumentation is constantly being updated or added to, so these descriptions are necessarily general.

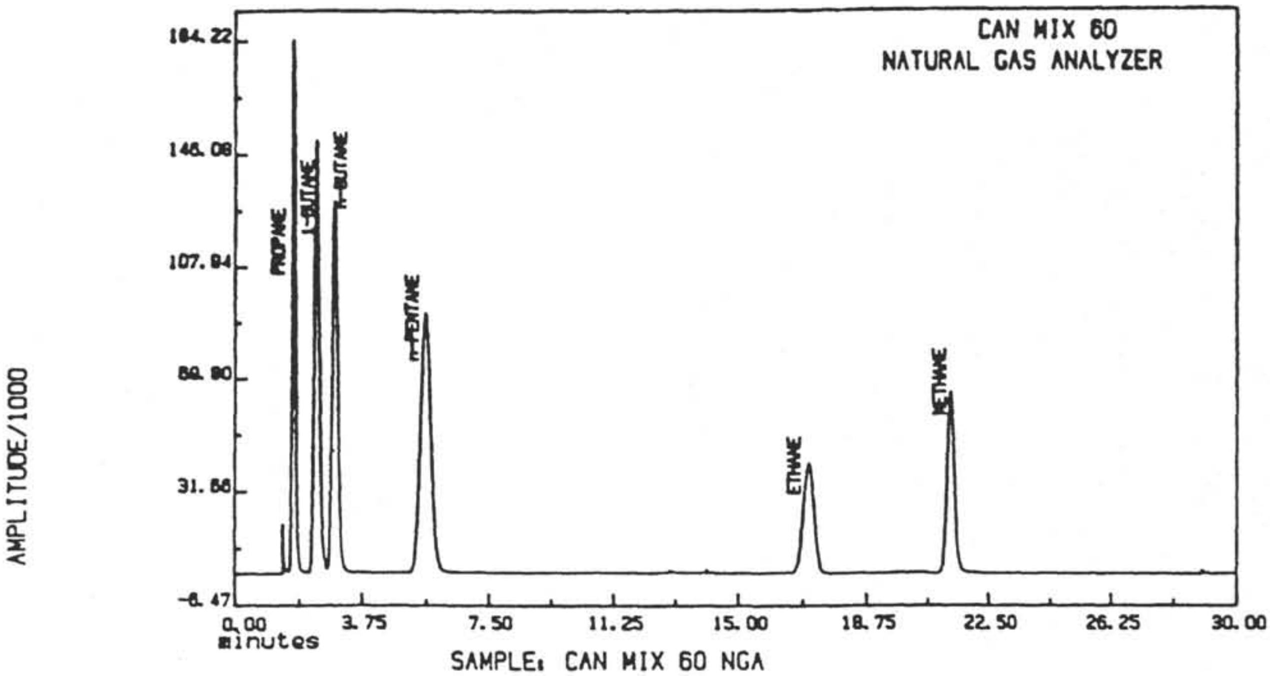
Natural Gas Analyzer (NGA)

The NGA is a special option (Option 820) for the H-P 5890A gas chromatograph. The system employs three columns and appropriate automatic valve switching to provide a complete and rapid determination of oxygen, nitrogen, methane, carbon dioxide, ethane, propane, the butanes, the pentanes, and the total hexane+ (C_{6+}) hydrocarbons. The method may be changed for the separation of the C_{6+} hydrocarbons or abbreviated for the analysis of "lean" gases. We suggest, however, that the NGA be run in the standard gas analysis mode and that the other H-P 5890A gas chromatograph be used for capillary gas chromatography. The NGA is controlled by the keyboard on the front right side of the GC. This keyboard controls the temperature settings of the ovens, detectors, and injection ports, along with the signal settings such as ranges and signal outputs. The manual located near the instrument gives details on programming the instrument, and a card located on the left side of the GC in the side door provides a quick reference to the control panel. Control of the three valves is accomplished by using the H-P 3392 Integrator. The NGA is interfaced through LAS to the H-P-1000 mainframe computer. This computer accepts raw data from the GC and stores these data in a result file unique to that sample. This procedure permits different analyses of data from the same sample and provides the capability to plot the file on an H-P 7470A Plotter. Example chromatograms are shown in Figure 13.

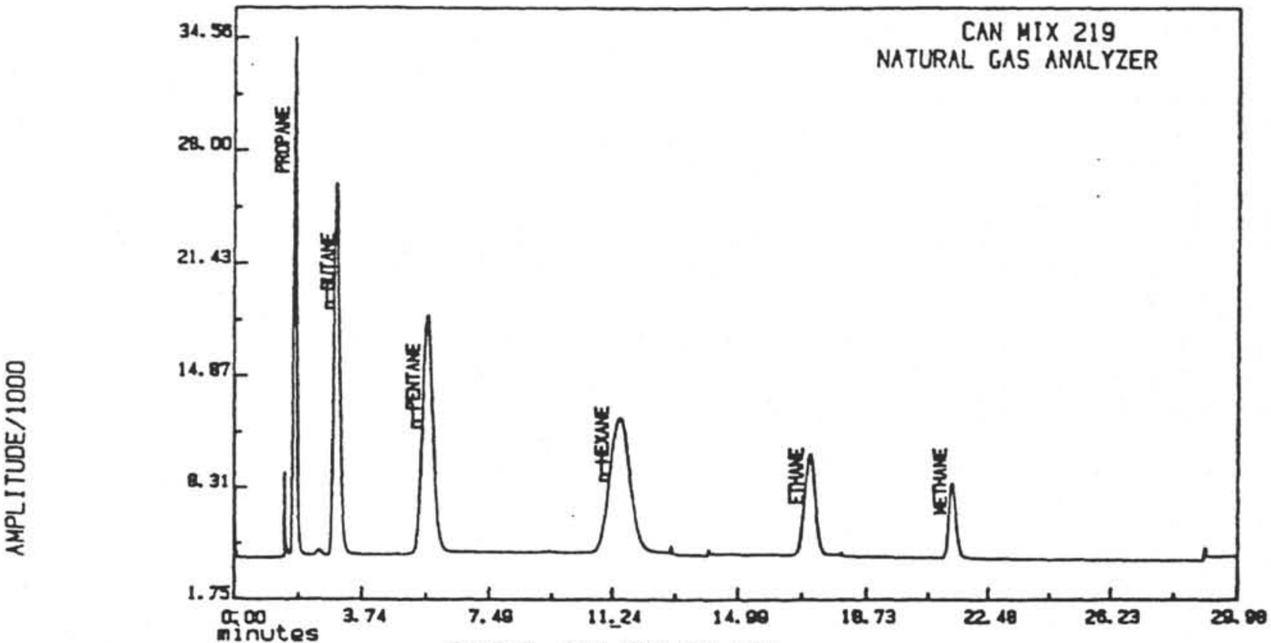
Hewlett-Packard 5890A Gas Chromatograph

This instrument provides numerous choices among inlets, columns, and detectors through inlet lines and adapters. Packed or capillary columns can be used without sacrificing performance. This instrument is mainly for high-resolution gas chromatography. There are two detectors, flame ionization (FID) and thermal conductivity (TCD), and two inlet ports. Either detector can be used with packed or capillary columns. Gas chromatographic peaks are integrated on an H-P 3392 integrator and on LAS.

The high-resolution capillary capability permits real time evaluation of heavy hydrocarbons. The columns available on the ship are H-P Ultra performance capillary columns (0.20mm internal diameter) coated with a 0.11 thickness of cross linked methyl silicone. A typical injection volume is 2 microliters. An example chromatogram (FID) of a standard mixture is shown in Figure 14.



```
          SAMPLE: CAN MIX 60 NGA
          ANALYZED: Sun Jul 14, 1985  1:12:24 am
RESULT: /DATA/LOOP/RESULT/CANMIX600.RES
```



```
          SAMPLE: CAN MIX 219 NGA
          ANALYZED: Mon Jul 15, 1985 12:56:31 am
RESULT: /DATA/LOOP/RESULT/CANMIX2190.RES
```

Figure 13. Example of CPLOT output of a standard gas sample analyzed with the Natural Gas Analyzer.

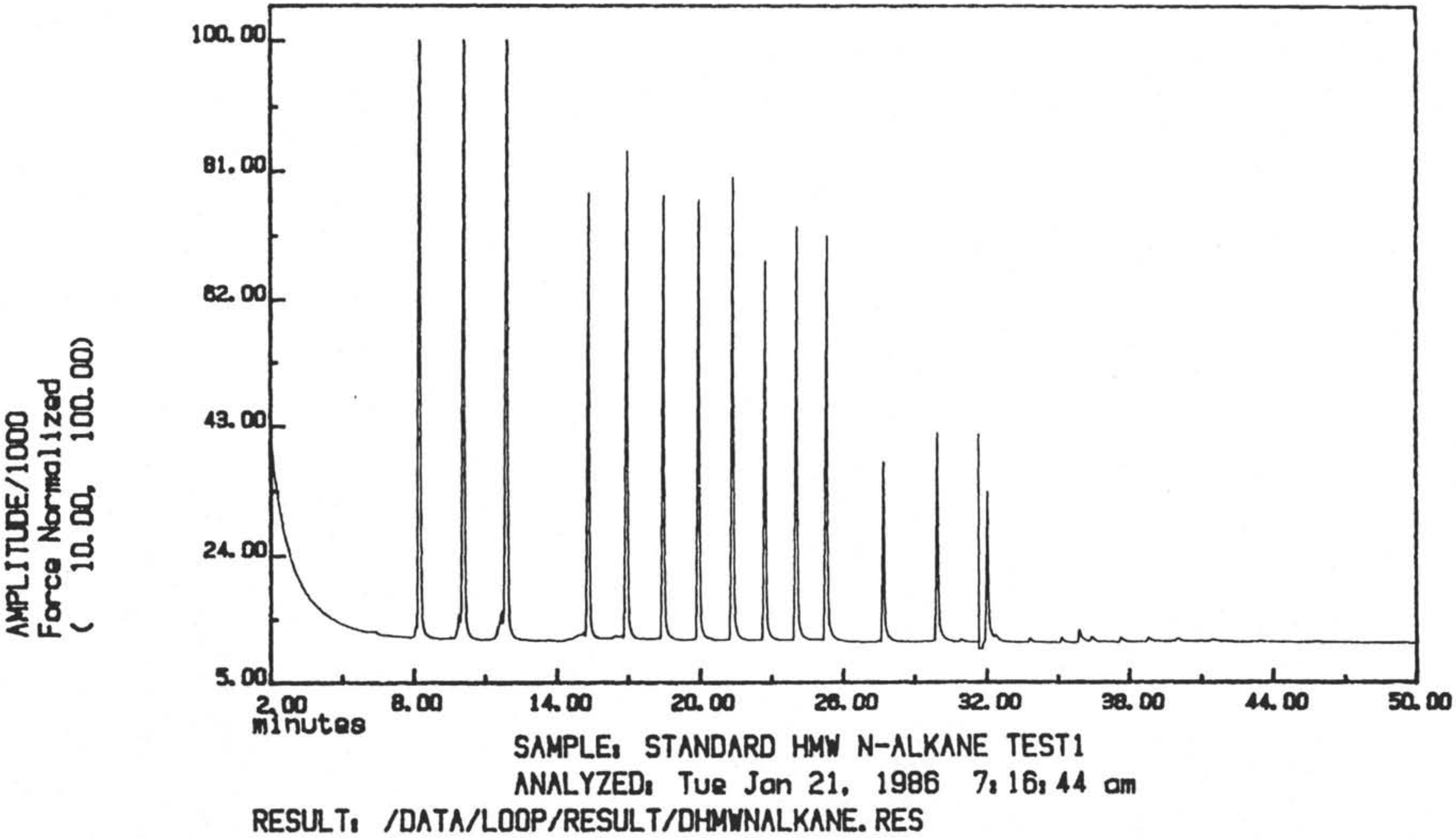


Figure 14. Example of CPLOT output of a standard mixture of n-alkanes analyzed by capillary gas chromatography.

Chromatographic peaks are integrated as above. The GC conditions for this analysis were shown in table 2 (main text).

Carle Gas Chromatograph

This instrument is a basic gas chromatograph which produces rapid analyses of gas up to molecular weight C_{3+}. In contrast to the more sophisticated NGA, it is intended to be the workhorse for on-line safety monitoring. The instrument is controlled and results are computed by a HP integrator. At the time of writing, the instrument underwent its first trial, and we do not have any information on performance.

Laboratory Automation System (LAS)

LAS is the software system that accepts digital data from the gas chromatographs and ion chromatographs. This system has been designed to help process the generated data into both tables and chromatographic plots. The software is used in a screen dialog mode; the user controls the program with a pointer and 8 soft keys. LAS stores the acquired digitized data from each chromatographic run in a unique result file as designated by the operator. Methods are set up to analyze the raw data; these methods are used to name peaks, to determine concentrations based on areas of individual peaks, to calculate total sample concentration, and to store this information in a processed file which can be used in CPLOT.

Chromatographic Plotting Program (CPLOT)

CPLOT is a comprehensive chromatogram plotting program for use with the LAS system. CPLOT allows the manipulation of the collected data to enhance or suppress the signal, to analyze a chosen time window, and to calculate area. CPLOT is controlled through 8 soft keys, 3 main menus, and 10 specialty menus. Only LAS result files and method files may be used in CPLOT. With this system raw data are never lost, and they can be plotted in numerous ways. Figures 13 and 14 were generated utilizing CPLOT.

Rock-Eval II with TOC

Rock-Eval is a whole rock or sediment pyrolysis system used to ascertain the type and maturity of organic matter and to estimate petroleum potential. The pyrolysis technique involves a microprocessor controlled temperature program that causes the release of the light-end hydrocarbons (oil/gas shows), recorded as a peak called S_1, and the release of hydrocarbon by thermal cracking of the kerogen matrix producing peak S_2. During the pyrolysis of the sediment CO_2 produced from pyrolysis of kerogen is indicated as peak S_3, and is trapped only between the initial starting temperature and 390°C; this trapping avoids other sources of CO_2 such as carbonate, especially siderite which is the most labile carbonate. A fourth parameter is T_{max} which is the pyrolysis temperature at which the S_2 peak reaches a maximum. In a second oven, the total organic carbon (TOC) is measured by combustion in an oxygen atmosphere. Rock-Eval automatically prints the results on a pyrogram (text, Fig. 9), in a data table (text, Table 3), and in a bar graph.

A series of standards with a wide range of maturity and organic carbon concentrations is available in the laboratory. The standard sample size is 100 mg. If the samples are very rich in organic matter, a smaller sample size may be used or samples are diluted with quartz sand.

Coulometrics 5030 Carbonate Carbon Apparatus, 5020 TC Apparatus and components for liquid samples

The Coulometrics carbon analyzer rapidly and accurately determines CO_2 from a variety of sources. The Coulometrics Model 5010 CO_2 Coulometer, which is the detector for the Carbonate Carbon Apparatus, is filled with ethanolamine and an indicator. When gas is passed through the solution, CO_2 is quantitatively absorbed and is converted to a strong acid by the ethanolamine. The coulometer electrically generates a base to return the indicator color to the starting color. Results for carbonate carbon are given in micrograms of carbon and percent $CaCO_3$. CO_2 is generated by treatment of the sediment with HC1 and gentle heating; the evolved CO_2 is transferred to the coulometer by a purified air stream. Analysis time is 3 to 7 minutes. For TC measurements, the sample is combusted at $950^{\circ}C$-$1000^{\circ}C$, converting mineral and organic carbon to CO_2. Interfering gases (SO_2, SO_3, NO_x etc.) are removed by a series of chemical scrubbers. Both total carbon (by combustion at $950^{\circ}C$ after direct injection) and inorganic carbon (by acidification to pH 2) can be determined in liquid samples (pore waters). Organic carbon content for solid and liquid samples is computed by difference.

Perkin Elmer CHN - ELEMENTAL ANALYZER

The model 240C Elemental Analyzer determines carbon, sulfur, and nitrogen in sediment samples, as well as H, C, and N concentrations in kerogen extracts prepared by HF digestion of sediments or organic substances. Samples are combusted at approximately 950° C in pure oxygen; the combustion products are then trapped and successively quantified in a thermal conductivity detector. Quantitative results are obtained by calibration with appropriate standards. The analysis of H in sediments is not possible, because hydrated clay mineral interlayers release H_2O during combustion which is recorded as H.

2. Data Sheets

Results of geochemical measurements are recorded onboard ship on data sheets. These are used after the cruise to enter results into the computer by shorebased personnel, thereby establishing a data base accessible to the entire scientific community. Recording of results and methods usually is performed by the Chemical Technicians at the termination of analyses for one hole. The following are samples of these data sheets for $CaCO_3$, CHN analyses, Rock-Eval pyrolysis, and gas chromatography.

ODP
$CaCO_3$ SUMMARY

LEG	SUB	SITE	HOLE

STANDARDS: ______ g 99 % $CaCO_3$ = ______ lbs. press.
______ ______
______ ______
______ ______
______ ______
______ ______
slope= ______ y intercept ______

Remarks:

* for Coulometrics : % Carbon X 8.33 = % $CaCO_3$

	CORE	SEC.	INTERVAL (cm)	DEPTH (m)	COULO-METRICS*/ BOMB (C/B)	WEIGHT (gm)	PRESSURE (psi)	% $CaCO_3$ [NOTE: May contain other types of carbonates]

FM 3006 REV. 8/85

These data will be processed into a computerized data base along with existing standardized data from other legs and will be accessible to the scientific community at large. RECORD MEASUREMENTS CAREFULLY, COMPLETELY, AND LEGIBLY.

LEG	SUB	SITE	HOLE

ODP
C H N SUMMARY

	CORE	SEC.	INTERVAL (cm)	DEPTH (m)	% ORGANIC CARBON Dry Sed. Wt.	% INORGANIC CARBON	% TOTAL CARBON	% HYDROGEN	% NITROGEN

Remarks

%Organic Carbon, Dry Sed. wt. = [100 - %CaCO3 x %Organic Carbon (Carbonate free, from CHN)]/100
%Inorganic carbon = Total Carbon (from CHN) - %Organic Carbon (from CHN)
%Inorganic Carbon x 8.33 = %Calcium Carbonate

FM 3003 REV. 8/85

These data are to be processed into a computerized data base along with existing standardized data from other legs and will be accessible to the scientific community at large. RECORD ALL MEASUREMENTS CAREFULLY, COMPLETELY, AND LEGIBLY.

LEG	SUB	SITE

ODP
ROCK EVALUATION SUMMARY

CORE	SEC.	INTERVAL (cm)	DEPTH (m)	WEIGHT (mg)	T-MAX (°C)	S 1	S 2	S 3	P I	S 2/S 3	P C	T O C	H I	O I

FM3005

These data are to be processed into a computerized data base along with existing standardized data from other legs and will be accessible to the scientific community at large. RECORD ALL MEASUREMENTS CAREFULLY, COMPLETELY, AND LEGIBLY.

REV. 8/8

ODP
GAS CHROMATOGRAPHY

LEG	SUB	SITE	HOLE	CORE	TYPE	SEC	INTERVAL	
							TOP	BOTT

	FID		TCD	
	AREA COUNTS	PPM	AREA COUNTS	PPM
C_1				
C_2				
C_3				
NC_4				
IC_4				
NC_5				
IC_5				
NC_6				
IC_6				
H_2S				
CO_2				
O_2				
N_2				
C_1/C_2				

CONDITIONS

Helium Pressure ______

Hydrogen Pressure ______

Air Pressure ______

Initial Temperature ______

Final Temperature ______

Column Pressure ______

Injection Temp. TCD ______

Injection Temp. FID ______

Range ______

Detector Temp. TCD ______

Detector Temp. FID ______

Sample Amount ______

Loop Size ______

Date ______

Time ______

COMMENTS

FM3002

These data are to be processed into a computerized data base along with existing standardized data from other legs and will be accessible to the scientific community at large. RECORD ALL MEASUREMENTS CAREFULLY, COMPLETELY, AND LEGIBLY.

REV. 4/22

APPENDIX B

Section 1. Index of Organic Geochemistry Information Published in the DSDP Initial Reports, organized by compound type.

Compound	References[1]
ACIDS:	
Carboxylic acids	20, 114, 144, 160, 174, 194, 220, 229, 265
Hydroxy acids	18, 20, 144, 160, 174, 229
Branched isoprenoid acids	18, 20, 101, 103, 105, 144, 160, 174, 184, 194, 229
Naphthenic acids	25, 26
Normal saturated fatty acids	18, 51, 101, 103-109, 111-114, 125, 134, 138, 158, 160, 174, 188, 194, 195, 200, 201, 216, 218, 220, 221, 229, 245, 248, 264, 271, 302
Cyclic terpenoid acids	20, 99, 101-105, 116, 125, 138, 144, 158, 160, 188, 201, 221, 229, 302
Unsaturated acids	18, 20, 114, 144, 160, 229
ALCOHOLS:	
Normal fatty alcohols	18, 51, 194, 197, 220, 229, 245, 264, 271
Branched/cyclic	106, 108, 111, 174, 194, 197, 220, 229, 231, 264
AMINO COMPOUNDS:	
Amino acids	3-5, 50, 91, 118, 119, 223, 236
Amino sugars	50, 69, 91, 226
Amines	50
ASPHALTENES, ASPHALITICS, NSO:	21, 27-29, 31, 32, 36, 39, 40, 48,

55-57, 70, 73, 76, 77, 80, 89, 90, 92, 123, 127-130, 132, 142, 151, 152, 157, 170, 171, 181, 184, 187, 191, 201, 211, 212, 214, 218, 227, 233, 235, 238, 239, 241, 242, 246, 253, 255, 262, 266, 273, 275, 280, 288, 290, 293

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	300, 301, 302, 308, 310
C_1-C_8	8, 23, 30, 33, 46, 47, 55, 60-62, 78, 79, 81, 83, 84, 85, 86, 87, 88, 89, 90, 92, 94, 120, 124, 133, 139, 143, 154, 155, 168, 170, 172, 173, 196, 198, 204, 206, 207, 208, 210, 213, 228, 232, 240, 246, 247, 249-251, 250-252, 263, 269, 279, 289, 296, 298, 299, 301, 303, 308, 310
C_4-C_{10}	33, 55, 57-59, 70, 73, 77, 78, 82, 90, 124, 151, 250
C_{10+} or C_{15+}	2, 18, 20, 21, 24, 27-29, 31, 32, 36, 38, 40, 47, 48, 55-57, 70, 73, 74, 76-78, 80, 83, 85, 89-92, 100-114, 116, 118, 122, 123, 125, 127, 129, 130, 132, 134, 136, 138, 140, 142, 144, 145, 151, 152, 156, 157, 158, 160, 163, 166, 169, 170, 171, 174, 180, 181, 184, 185, 187, 188, 191, 194, 195, 197, 200, 201, 211, 212, 214, 216, 218, 220, 221, 229, 233, 238, 239, 241, 244-246, 248, 255, 262, 264, 265, 270-273, 275-277, 280, 290, 291, 293, 294, 300, 302
Alkenes (unsaturated)	2, 20, 29, 101, 104, 105, 11, 123, 127, 136, 138, 142, 144, 157, 160, 163, 173, 174, 194, 197, 207, 218, 228, 229, 238, 239, 240, 255, 263, 265, 269, 270, 272, 276, 288, 289, 303
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Nitrogen	201
Hydrogen	201, 210, 297, 299, 310
Oxygen	242, 279, 297, 299, 310
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[1] See Section 4 of this appendix for full reference citations.

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5	34, 35	2	74
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	36, 42	2	119
6	47, 49, 50	3	74
	47, 49, 50, 51, 52, 53, 55, 56, 58	13	107
	47	1	119
7	62, 64, 65, 66	8	107
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8	73, 74, 75	4	75
	72, 73, 74, 75	6	106
9	78, 80, 82, 83, 84	6	76
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	82	1	119
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	88, 90, 91	14	23
	90, 92	2	98
	92	1	99
11	102, 103, 104, 106B	19	94
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	102, 104, 106	8	23
	105	1	98
	105	1	99
12	111, 112, 116, 118, 119	153	96
	112, 114	2	109
	112, 114	2	98
13	134	1	78
	128, 130, 134	4	109
	128	3	23
	128, 130	3	98
	125	1	67

14	138, 144	6	113
	144	2	23
	138, 144	5	98
	144	2	16
15	147, 154	12	34
	147	3	111
	147	1	51
	147	3	50
	147	7	14
	148	12	3
	147	8	77
	147	4	98
18	174, 176, 180	29	79
	174, 176	9	23
	174, 176, 180	29	86
19	185, 186, 189, 191	19	80
	185, 186, 189, 191	4	23
	185, 186, 189, 191	19	86
20	198	1	16
21	204, 210	4	81
	204, 210	4	86
22	217, 218	10	82
	217, 218	4	55
	217, 218	10	115
	217	4	110
	217, 218	8	41
23	222, 229	6	85
	229	1	56
	222, 229	6	86
24	231	3	21
	231, 232	9	83
	232, 233	5	56
	233	4	41
	231, 232	9	86
26	250, 254, 257	3	41
	252, 253, 254, 256, 257, 258	72	19
	250	1	16
27	259, 263	2	41
	262	11	84
	262	11	86

	259, 263	2	57
	259, 263	2	16
28	267	1	41
	271, 272, 273	21	86
	265	1	57
29	278	12	87
	280, 281, 282	15	57
	280, 281	5	16
	280, 281, 282	12	42
31	297, 298	21	1
	299, 302	11	15
	200, 302	11	43
36	327A, 330	10	24
	330	6	158
	327A, 330, 511		238
	327, 330, 356, 357, 361, 363, 511, 530A	277	267
37	332A, 333	6	5
38	336, 338, 341, 343, 344, 345, 346	36	13
	338, 339, 341, 344, 346, 348, 349	42	35
	338, 341, 342, 343, 344, 346, 348, 350	39	52
	339, 345	4	100
	336, 338, 345, 348	13	58
	341	34	92
	336	27	17
39	354	2	102
	356	10	47
	356	1	9
	356, 357, 327, 330, 361, 511, 530A, 363	277	267
40	360, 361, 362, 362A, 363, 364, 3365	136	47
	362	4	18
	361, 362, 373, 375	19	9
	361, 364	10	59
	361, 362, 362A	40	37
	364	3	103
	361, 362, 364	8	95
	361, 362, 363, 364, 365	29	65
	364	1	105
	361	15	156
	362	19	156
	361, 363, 327, 330, 356, 3367, 511, 530A	277	267
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	367, 368, 369, 369A, 370	28	10
	367, 368	30	8
	368	11	36
	367, 369	3	101
	367, 368, 369, 370	6	60
	368, 369A	22	30
	367, 368	7	29
	370, 415, 415A, 416A	178	149
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	374	23	49
	372, 376	3	4
	376	4	38
	376, 378	4	67
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	379A, 379B, 380A, 380B, 381	44	46
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[1] See Section 4 of this Appendix for complete reference citation.

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1	DSDP	1	340-347	127
2	DSDP	2	319-321	37
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4	Pimm	4	307-314	225
5	Vallier	5	431-440	286
6	Pimm	6	739-752	422
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10	Boyce	10	641-642	93
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16	Bode, Cronan	16	521-528	732
17	Bode	17	927-930	376
18	Bode	18	1069-1076	788
19	Bode	19	663-665	217
20	Bode	20	741-742	80
23	Bode	23	1131-1135	320
24	Bode	24	1155-1156	78
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27	Bode	27	499-502	329
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35	Cameron	35	755-756	38
36	Cameron	36	1047-1050	144
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42A	Sigl	42 Pt 1	1221-1224	392
43	Cameron	43	1043-1047	233
44	Myers	44	983-986	360
44, 76	Katz	76	463-468	53
45	Bode	45	379-380	45
47	Kendrick, Hood,	47 Pt 2	547-551	18

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47	Erdman, Schorno	47 Pt 2	553-559	58
47	Whelan, Hunt	47 Pt 2	561-563	15
47A	Kaban'kov, et al. Basov, et al.	47 Pt 1	579-590	2
47A	Cornford, et al.	47 Pt 1	511-522	44
47A	Deroo	47 Pt 1	523-529	9
47A	Whelan	47 Pt 1	531-539	18
47A	Simoneit, Mazurek	47 Pt 1	541-545	3
47A	Baker, Palmer	47 Pt 1	547-551	9
47B	Doerenkamp, Robert	47 Pt 2	529-531	25
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47B	Cornford	47 Pt 2	523-527	23
47B	Pearson, Dow	47 Pt 2	533-537	23
47B	Johnson, McIver, Rogers	47 Pt 2	543-546	86
47B	Kendrick et al.	47 Pt 2	547-551	18
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47B	Whelan, Hunt	47 Pt 2	561-563	15
47B	Simoneit, Mazurek	47 Pt 2	565-570	7
47B	Palmer, Baker	47 Pt 2	571-575	13
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48	Baker, Palmer	48	931-933	8
48	Simoneit	48	935-941	4
48	Whelan, Hunt	48	943-945	6
48	Erdman, Schorno	48	947-950	12
48	Kendrick, Hood, Castano	48	951-954	11
48	Pearson,	48	955-957	8

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48	Barnes et al.	48	965-975	4
48	Doran, Johnson, et al.	48	977-992	37
49	White, Bode	49	873-882	578
50, 41	Boutefeu	50	555-566	178
48	Boutefeu et al.	48	567-573	24
50	Galimov, Kodina, et al.	50	575-600	38
50	Claypool, Baysinger	50	605-608	8
50	Cornford	50	609-614	9
48	Galimov et al.	48	615-622	49
50	Whelan, Hunt	50	623-624	8
50	Schorno, Erdman	50	625-627	8
50	Deroo, Herbin, et al.	50	629-635	6
50	Simoneit	50	637-641	6
50	Palmer, Baker	50	643-645	10
50	Brassell, Comet, et al.	50	647-664	3
50	Bode	50	835	56
51-53	White	51-53 Pt 1	715-718	127
51-53	Deroo, Herbin, et al.	51-53 Pt 2	737-745	32
55	Jackson, Koisumi, et al.	55	861-862	25
56, 57	Rullkoetter, Cornford, et al.	56-57 Pt 2	1291-1304	19
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56, 57	Gilbert, Summerhayes,	56-57 Pt 2	1327-1330	27

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56	Louda, Palmer, Baker	56-57 Pt 2	1391-1396	12
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58	Waples	58	741-743	48
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61	Simoneit	61	627-629	2
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62	Dean	62	869-876	118
62	Dean, Claypool, Thiede	62	877-890	34
62	Timofeev, Bogolyubova	62	891-901	9
62	Melieres, Deroo, Herbin	62	903-921	123
62	Comet et al.	62	923-937	1
62	Simoneit	62	939-942	1

63	Gilbert, Summerhayes	63	757-761	5
63	McEvoy et al.	63	763-774	2
63	Whelan, Hunt	63	775-784	27
63	Louda, Baker	63	785-818	21
63	Rullkoetter, Dick, Welte	63	819-836	12
63	Simoneit, Mazurek	63	837-853	10
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64	Oremland et al.	64 Pt 2	759-762	12
64	Whelan, Hunt	64 Pt 2	763-779	43
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64	Baker, Louda	64 Pt 2	789-814	42
64	Schoell	64 Pt 2	815-817	21
64	Galimov, Kodina, et al.	64 Pt 2	819-836	26
64	Rullkoetter, v.d. Dick, Welte	64 Pt 2	837-853	20
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64	Gilbert, Summerhayes	64 Pt 2	865-870	41
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64	Swain, Bratt	64 Pt 2	881-882	10
64	Simoneit, Philp	64 Pt 2	883-904	33
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64	Peters, Simoneit	64 Pt 2	925-931	57
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66	Shipley	66	547-555	9
66	Brassell, Eglinton, Maxwell	66	557-580	2
66	Chambers, Erdman	66	581-585	22
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67	Summerhayes, Gilbert	67	595-599	7
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69	Whelan, Hunt	69	443-450	46
71	Deroo, Herbin, Roucache	71 Pt 2	1001-1013	206
71	v.d. Dick, Rullkoetter, Welte	71 Pt 2	1015-1032	95
71	Schaeffer, v.d. Dick, Leythaeuser	71 Pt 2	1033-1043	56
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71	Parker, Arthur, et al.	71 Pt 2	1051-1070	36
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72	Meyers, Dunham	72	833-839	5
72	Padilha de Quadros, et al.	72	841-845	28
73	Herbin, Deroo	73	537-538	41
73	Bode	73	789-790	135
74	Meyers,	74	731-736	6

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75	Gardner, Dean, Wilson	75 Pt 2	905-921	585
75	Meyers, Brassell, Huc	75 Pt 2	967-981	334
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75	Gilbert	75 Pt 2	1035-1049	277
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75	Meyers, Dunham	75 Pt 2	1089-1095	4
76	Brooks, Barnard, et al.	76	377-389	24
76	Claypool	76	391-402	15
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76	Kagami, Ishizuki and Aoki	76	429-436	2
76	Chamley, Debrabant et al.	76	437-451	37
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77	Palacas, King et al.	77	477-488	6
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77	Bode	77	739-741	161
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79	Deroo, Herbin and Roucache	79	721-741	300
79	Schaeffer et al.	79	743-773	54
79	Rullkoetter et al.	79	775-806	31
79	Simoneit et al.	79	807-824	15
80	Waples and Cunningham	80 Pt 2	949-968	500
80	Cunningham and Gilbert	80 Pt 2	969-981	71
80	Hartung et al.	80 Pt 2	983-991	6
80	Waples	80 Pt 2	993-997	26
84	Kvenvolden and McDonald	84	667-682	10
84	Kennicutt, Brooks et al.	84	705-717	67
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90	Mycke et al.	90	1265-1269	46

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(Numbers refer to references cited in Sections 1 & 2 of this appendix)

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METHANE AND OTHER HYDROCARBON GASES IN MARINE SEDIMENT[1]

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INTRODUCTION

Hydrocarbon gases are common in marine sediment accumulating in present-day oceans. Such gases originate from the decomposition of organic matter by biochemical and chemical processes. We consider seven hydrocarbon gases that occur in marine sediment (Table 1). In addition, inorganic gases such as nitrogen (N_2), argon (Ar), carbon dioxide (CO_2), and helium (He) are present, but usually as minor or trace components in natural gas. These will not be discussed here.

Methane (C_1) is almost always the dominant component of the natural gas mixtures. Usually accompanying C_1 are other hydrocarbon gases, including ethane (C_2), propane (C_3), isobutane (i-C_4), and normal butane (*n*-C_4), that are present in variable amounts from traces to 30–40 percent collectively. Marine sediments also contain volatile hydrocarbons of higher molecular weight, e.g. C_5 through at least C_7 (Hunt 1975), but our discussion is confined to permanent gas hydrocarbons C_1 through C_4. In addition to gaseous alkanes, the alkenes, ethene ($C_{2=}$) and propene ($C_{3=}$), are found also, but mainly in sediment near the seafloor and in the overlying water column.

There are three main stages of natural gas formation during the burial history of sediment. The earliest stage is biological C_1 formation, which

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Table 1 Hydrocarbon gases in marine sediment

Name	Symbol	Molecular formula	Molecular weight
Methane	C_1	CH_4	16
Ethene	$C_{2=}$	C_2H_4	28
Ethane	C_2	C_2H_6	30
Propene	$C_{3=}$	C_3H_6	42
Propane	C_3	C_3H_8	44
Isobutane	i-C_4	C_4H_{10}	58
n-Butane	*n*-C_4	C_4H_{10}	58

occurs at low temperatures (< 50°C) under certain environmental conditions. The next stage is early thermogenic (nonbiological) gas formation, in which the whole series of gaseous and liquid hydrocarbons are formed at rates that become geologically significant when burial temperatures are in the range of 80–120°C. Late thermogenic C_1-rich gas is produced during the last stage of gas formation, at temperatures higher than about 150°C at which previously formed heavier hydrocarbons are converted to C_1. Natural gas formed during each of these stages has a characteristic chemical and isotopic composition.

Cold bottom water ($\simeq 2°C$) and thin sediment cover (< 1 km) over most of the deep ocean basins prevent attainment in the sediment of the temperatures required for significant nonbiological gas formation, except in unusual circumstances. Only at continental margins or at active ocean ridges are sediment temperatures achieved that permit significant nonbiological gas generation from high-temperature (80–150°C) decomposition of organic matter. As a consequence, the low-temperature biological decomposition of organic matter is the most important C_1-generating process operating in marine sediments accumulating in present-day oceans.

C_1 generation in nonmarine environments, e.g. "marsh gas," is an obvious consequence of organic decay under anaerobic conditions. However, prior to the advent of deep coring of the seafloor by the Deep Sea Drilling Project (DSDP), the extent of C_1 occurrence in the marine environment was not widely appreciated or understood (Atkinson & Richards 1967). Gassy marine sediments occasionally have been reported in coring operations in which penetration was limited to the upper 5 m of surface sediment (Revelle 1950, Emery & Hoggan 1958, Reeburgh 1969, 1976, 1980, Nissenbaum et al 1972, Rashid et al 1975, Martens & Berner 1977), but gassy sediments are more commonly found in DSDP rotary coring, at depths previously unattainable by conventional gravity or piston coring.

C_1 GENERATION AND CONSUMPTION PROCESSES

Sedimentary C_1 is formed by both biological and nonbiological decomposition of buried organic matter. Anaerobic microorganisms produce relatively pure C_1 enriched in the light isotope ^{12}C. C_1, as well as other alkane hydrocarbons, is produced by nonbiological, spontaneous decomposition of organic matter at rates that increase in an exponential fashion with increasing temperatures. At average Earth-surface temperatures (10–25°C), the rate of nonbiological hydrocarbon formation is extremely slow, and these hydrocarbons probably do not make a volumetrically significant contribution to economic gas occurrence, even when the process has continued over geological time periods. Only when organic matter is heated to temperatures of about 100°C (Frank et al 1974) does nonbiological gas formation occur at rates that are significant on the time-scale of the development period of sedimentary basins (10^8 yr).

Hydrocarbons (C_1 in particular) are subject to rapid biological oxidation in aqueous systems that contain dissolved O_2 (Rudd et al 1974, Patt et al 1974, Rudd & Hamilton 1975, 1978, Jannasch 1975, Rudd 1980). In addition, there is evidence that C_1 can be anaerobically oxidized in conjunction with active sulfate reduction (Reeburgh 1976, 1980, Reeburgh & Heggie 1977, Barnes & Goldberg 1976, Kosiur & Warford 1979). The processes of aerobic oxidation of hydrocarbons are well understood (McKenna & Kallio 1965), but the mechanisms for anaerobic degradation are still a matter of debate. In general, C_1 content in aerobic and sulfate-containing sediment is low ($< 10^{-4}$ standard volumes of gas per volume of sediment, v/v) and is most properly viewed as a result of the balance between C_1 production or influx, and C_1 consumption. In anoxic, sulfate-free, or low-sulfate sediment beneath a water column of sufficient depth to inhibit bubble formation, C_1 content can be high (0.05–2 v/v) and C_1 loss is by upward diffusion.

Biological Processes

The breakdown of organic matter in anoxic environments involves a complex sequence of processes symbolized in Figure 1, which is modified and expanded after Mah et al (1977). Dead organic tissue is dissaggregated and hydrolytically decomposed to yield the constituent biopolymers–cellulose, alginate, proteins, and lipids. The more labile of these biopolymers are hydrolyzed to yield the biomonomers (sugars, uronic acids, amino acids, fatty acids), which in turn are decomposed by fermentation and anaerobic oxidation reactions to give 2-, 3-, and 4-carbon organic compounds (acids, alcohols, aldehydes, etc). These short-chain organic compounds are further oxidized to CO_2, with consequent production of electrons or hydrogen. Continued metabolic activity depends on the removal of electrons by the biologically mediated reduction of certain inorganic compounds known as *electron acceptors*. A variety of multivalent elements (including O, Fe, Mn, N, S, C) can act as electron acceptors. In the interstitial waters of anoxic marine sediments, dissolved SO_4^{2-} and CO_2 are the most important electron acceptor compounds.

C_1 in low-temperature marine environments probably is produced from a limited range of substrates: H_2+CO_2, acetate, and formate (Mah et al 1977). Other compounds (methanol, trimethylamine, methionine, methyl mercaptan, and dimethyl sulfide) apparently can provide alternative carbon substrates for methanogenesis under unusual environmental conditions (Zinder & Brock 1978, Oremland et al 1982a). Of the more common substrates, formate is believed to be more readily converted to H_2+CO_2 than fermented to C_1 (Hungate et al 1970). With respect to the relative importance of acetate vs H_2+CO_2 as substrates for methanogenesis,

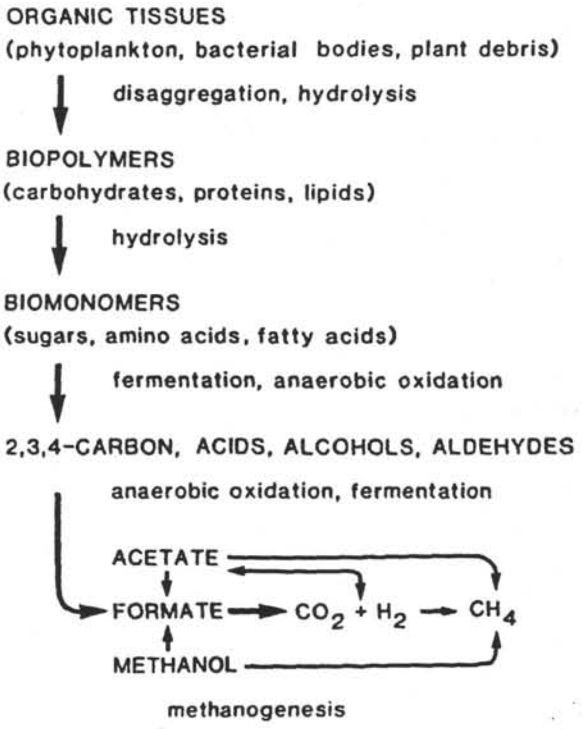

Figure 1 Sequence of organic matter degradation reactions in marine sediments.

environmental conditions also are important (Mah et al 1977, Mountfort & Asher 1978). Evidence for the importance of acetate fermentation in shallow-water, coastal lagoons is conflicting (Sørensen et al 1981, Sansone & Martens 1981). In deeper-water marine sediments, the evidence favors CO_2 reduction as the dominant methanogenic process; acetate fermentation is an energetically less favorable process (Zeikus 1977). Radiolabeling experiments have shown that acetate is anaerobically oxidized to CO_2 prior to C_1-generation in Santa Barbara Basin sediments (Warford et al 1979), and that 55–99% of C_1 in Baltic Sea sediments was formed via CO_2 reduction (Lein et al 1981).

Sulfate-reducing bacteria are believed to compete so favorably with CO_2-reducing microorganisms for available electron donors or hydrogen that C_1 production can be inhibited in the presence of dissolved SO_4^{2-} (Claypool & Kaplan 1974, Martens & Berner 1974, Winfrey & Zeikus 1977, Abram & Nedwell 1978, Sansone & Martens 1981). Apparently, biological C_1 production does not occur at optimum rates in most marine sediments until more than 80% of the dissolved SO_4^{2-} is depleted (Nikaido 1977). The depth of SO_4^{2-} depletion depends on the relative rates of biological processes and replenishment of SO_4^{2-} from overlying sea water, and varies from as little as a few centimeters to as much as 200 m. In marine environments, sediment immediately beneath the effective depth of SO_4^{2-} depletion invariably contains abundant C_1, and displays other geochemical changes indicating that rapid C_1 generation is taking place (Claypool & Kaplan 1974). Thus, a separation exists between sediment zones where C_1 production and SO_4^{2-} reduction are the dominant terminal processes. The two processes are not, however, mutually exclusive in the strictest sense (Oremland & Taylor 1978, Mountfort et al 1980, Oremland et al 1982b).

The apparent inhibition of methanogenesis by SO_4^{2-} is usually rationalized in terms of a competitive advantage conferred by greater relative free-energy yield for SO_4^{2-} reduction (Claypool & Kaplan 1974, Berner 1980). However, a more direct, mechanistic explanation involves the observed, more favorable kinetic parameters for H_2 utilization possessed by SO_4^{2-}-reducing bacteria compared with methanogens (Kristjansson et al 1982). In this manner, SO_4^{2-} concentration determines the dominant anaerobic respiration process, whereas the actual rates of either process are affected by other factors controlling substrate availability (Winfrey et al 1981).

Concentration And Isotopic Depth Profiles

One of the main lines of evidence for sequential SO_4^{2-}-reducing and C_1-producing anoxic diagenetic processes related to the most energetically efficient available electron acceptor comes from studies of interstitial waters from marine sediments (Berner 1980). In particular, the depth distribution of dissolved sulfur and carbon species and their stable isotope ratios clearly indicate distinct zones of diagenesis. An idealized depth plot of the concentration and δ-values[2] for some of the dissolved carbon and sulfur species in the porewater of typical anoxic marine sediments is shown as Figure 2. The depth scale of Figure 2 is arbitrary in the sense that the units of depth can vary from 10^{-1} to 10^2 m, depending on several factors, the most important of which is the rate of sediment accumulation. Figure 2 is a generalized composite of porewater data from several deep-water depositional environments, but draws most heavily on data from the Astoria Fan (Claypool 1974) and the Blake Outer Ridge (Claypool & Threlkeld 1983).

The depth profile of dissolved sulfate shows a regular decrease from seawater concentrations near the seafloor to zero at an arbitrary depth of 2 units. Over this same depth interval, the $\delta^{34}S$ of residual sulfate increases from $+20^{\circ}/_{oo}$ to about $+50^{\circ}/_{oo}$. Dissolved CO_2 concentration increases as sulfate concentration decreases, and may reach values that are twice the original sulfate concentration in seawater (56 millimolar). Because the increased $\sum CO_2$ is derived from oxidation of organic matter, the $\delta^{13}C$ of $\sum CO_2$ decreases rapidly with sediment depth from seawater values of $0^{\circ}/_{oo}$ near the seafloor to the $\delta^{13}C$ range of organic carbon ($-25 \pm 2^{\circ}/_{oo}$) and remains at this value down to a depth of about 2 units.

At depths greater than 2 units in Figure 2, the $\delta^{13}C$ of $\sum CO_2$ shifts abruptly to heavier values as a consequence of the preferential removal of ^{12}C-enriched CO_2 to form C_1. At the depth at which sulfate goes to zero the concentration of $\sum CO_2$ also decreases, reflecting the onset of rapid C_1 generation. In addition, this depth (2 units) is usually the shallowest depth of readily observable C_1, as marked by the appearance of gas pockets in DSDP cores, or as reflected by greatly increased C_1 concentrations in the few studies of deep marine sediments in which quantitative measurements were permitted by the sampling methods (Emery & Hoggan 1958). The C_1 with the most negative $\delta^{13}C$ (-100 to $-90^{\circ}/_{oo}$) also occurs at the depth of the transition from SO_4^{2-} reduction to CO_2 reduction, or at a depth of 2 units in Figure 2. Isotopically heavier C_1 (more positive $\delta^{13}C$) occurs at greater depths because of progressive depletion of ^{12}C in the $\sum CO_2$ reservoir from which the C_1 is formed. At depths shallower than 2 units in Figure 2, the small amounts of C_1 present have more positive $\delta^{13}C$ values, indicating partial oxidation in the zone of sulfate reduction (Doose & Kaplan 1981, Brooks et al 1983). This oxidation process selectively removes

[2] Stable isotope ratios for carbon and sulfur are reported in the standard δ-notation, where $\delta(^{\circ}/_{oo}) = [(R_{sample}/R_{standard}) - 1] \times 10^3$, $R = {}^{13}C/{}^{12}C$ and ${}^{34}S/{}^{32}S$; and the standards are PDB marine carbonate and Cañon Diablo meteoritic troilite, respectively.

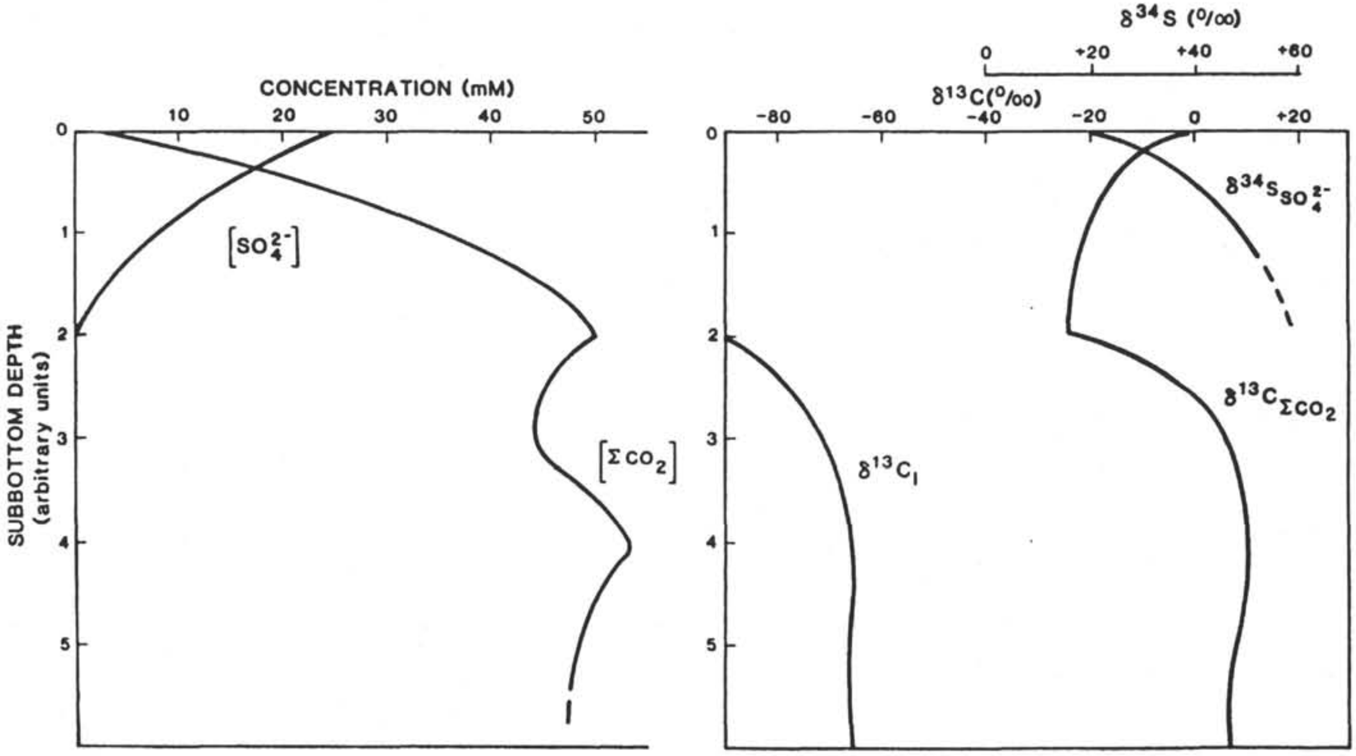

Figure 2 Generalized profiles of concentration and stable isotope ratio changes for dissolved sulfur and carbon species in anoxic marine sediments. Depth scale is arbitrary with depth units ranging from 10^{-1} to 10^{2} m.

^{12}C and leaves the residual C_1 relatively enriched ($\delta^{13}C$ of -50 to $-40°/_{oo}$, or heavier). A similar isotope effect has been documented for aerobic C_1 oxidation (Silverman & Oyama 1968, Coleman et al 1981, Barker & Fritz 1981).

The curve in Figure 2 representing $\sum CO_2$ concentration shows a second deeper maximum at a depth of 4 units, after the cessation of sulfate reduction and the onset of rapid C_1 generation. Because the porewater $\sum CO_2$ concentration at any depth is a consequence of the balance between processes adding and removing CO_2, this increased $\sum CO_2$ can be due either to a relative increase in the rate of CO_2 production or to a decrease in the rate of C_1 generation. The second maximum in $\sum CO_2$ concentration is due to continued or increased generation of CO_2 from decomposition of organic matter, as shown by the tendency of the $\delta^{13}C$ of $\sum CO_2$ to become lighter (more negative) at these depths (below 4 in Figure 2). Addition of isotopically light CO_2 ($\delta^{13}C = -25°/_{oo}$) at depth is sometimes also reflected in a tendency for the cumulative C_1 to become slightly lighter at these depths.

The depth-related changes described above are typical of anoxic marine sediments. These changes are the main evidence for the recognition of depositional and diagenetic sedimentary environments responsible for C_1 generation. Wherever the conditions discussed above do not exist, C_1 is absent or present only at background levels (10^{-8}–10^{-5} v/v).

Nonbiological Processes

Although microbiological processes appear to be by far the most important source of C_1 in sediments of ocean basins, nonbiological processes also contribute some C_1. Three types of nonbiological C_1-generating processes are considered: first, the nonbiological decomposition of sedimentary organic matter at low temperatures ($<75°C$); second, the high-temperature ($>75°C$) degradation of organic matter; and third, the outgassing of primordial C_1 from the mantle.

LOW-TEMPERATURE NONBIOLOGICAL C_1 The nonbiological decomposition of sedimentary organic matter forms the whole series of permanent gaseous alkane hydrocarbons (C_1, C_2, C_3, C_4, etc) in relative amounts that diminish regularly with increasing molecular size. The exact proportion of the various hydrocarbon gas components produced depends to some extent on the chemical composition of the organic matter being degraded. In general, C_1 is 5–20 times as abundant as C_2 in gases originating from nonbiological decomposition of organic matter.

C_1 of possible nonbiological origin is observable at levels of 10^{-8}–10^{-5} v/v in pelagic marine sediments with low organic matter content (C_{org}

< 0.2%) beneath the zone of surface biological activity (Claypool 1983). Microbiological C_1 is absent from such sediments because of the lack of metabolizable organic matter and the presence of alternative electron acceptors. C_1 of microbiological origin typically is present in marine sediments of continental slopes and rises, with organic carbon contents in the range of 0.5–1%. Higher contents of nonbiological hydrocarbons also are present in methanogenic sediments, but the low-temperature nonbiological C_1 is completely masked by biological C_1. However, because most C_{2+} hydrocarbons are not a direct product of the microbiological decomposition of organic matter, the approximate content of nonbiological C_1 in gas of predominantly biological origin is about ten times the level of C_2.

C_1 OF HIGH-TEMPERATURE ORIGIN Most sediments accumulating in present-day ocean basins have not been exposed to high temperatures. Therefore, the limited occurrence in marine sediments of C_1 originating from the apparent high-temperature decomposition of organic matter (i.e. $\delta^{13}C_1$ of -50 to -30°/₀₀) can be explained in one of two ways: either the gas was generated at a more distant high-temperature location and migrated into cooler marine sediments, or instead the gas was generated in sediments subjected to high temperatures sometime during their burial history.

Large parts of the ocean basins are underlain by sediment thicknesses in excess of 3 km, especially near continental margins. Organic matter in such deeply buried sediments could have generated hydrocarbons that then migrated into the sediments within 1 km of the seafloor. DSDP holes drilled above salt domes in the deep Gulf of Mexico on Legs 1 and 10 found gas of apparent thermogenic origin, which probably migrated up from greater depths along with the salt diapir (Erdman et al 1969, Claypool et al 1973). Other DSDP holes have been drilled in regions with anomalously high thermal gradients (e.g. Gulf of California), and C_1 of high-temperature thermogenic origin was found at relatively shallow depths of burial (Galimov & Simoneit 1982). The chemical and isotopic composition of gases sampled in the DSDP cores is briefly reviewed in a following section.

PRIMORDIAL C_1 Interest in C_1 gas of primordial origin has increased recently as a result of the observation that primordial gases (^3He, C_1, H_2) are being injected into the deep oceans from hydrothermal systems operating at active mid-ocean ridges (Welhan & Craig 1979, Lupton & Craig 1981). This has led to speculation that gas from similar sources may have natural resource implications (Gold 1979, Gold & Soter 1980). The occurrence of primordial C_1 in marine sediments has not been documented, but is probably minor. Gas with composition indicative of likely mantle origin ($C_1/^3He = 3$–10×10^6, $\delta^{13}C_1 = -19$‰) has been most clearly identified in solution in water ($C_1 = 10^{-3}$ v/v) issuing from fresh basalt at 21°N on the East Pacific Rise (Welhan 1980). At spreading centers where hydrothermal systems are operating through appreciable thicknesses of organic-matter-rich sediment, as in Guaymas Basin in the Gulf of California, the hydrocarbon gases in the sediment and those being injected into the water column have a composition indicating origin from organic matter decomposition (Simoneit & Lonsdale 1982).

In general, the flux of C_1 into marine sediments from low-temperature, nonbiological organic-matter decomposition and from outgassing of the Earth is so slow that only a highly efficient concentrating and trapping mechanism could bring about a recognizable accumulation of such gas. In addition, the fact that such gas would be dispersed at low concentrations in marine sediment makes it extremely difficult to study. Gas of high-temperature origin is relatively rare in sediments of present-day ocean basins, but is probably much more important than C_1 gas from the other two nonbiological processes mentioned.

OCCURRENCE OF C_1 AND ORIGIN AND OCCURRENCE OF OTHER HYDROCARBON GASES

Trace or minor amounts of the other hydrocarbon gases (C_2, C_3, and C_4) commonly are found associated with C_1 where sensitive detection techniques have been used in gas analyses. Emery & Hoggan (1958) showed that near-surface marine sediment (<4 m subbottom) from Santa Barbara Basin off southern California contains mainly C_1, but also small amounts (10^{-7}–10^{-4} v/v) of C_2, $C_{2=}$, C_3, i-C_4, and *n*-C_4, as well as volatile hydrocarbons to C_7. Their sampling procedures involved collection of large-volume samples and transfer of the sediment from the seafloor to the laboratory without exposing the core to air. This sampling technique compensated for the small amounts of C_2 through C_4 hydrocarbons and the relatively insensitive detection techniques, which discouraged any immediate follow-up of these kinds of measurements.

Gases in Near-Surface Sediment

Published research on the occurrence of C_2 through C_4 hydrocarbons in near-surface marine sediments languished for almost twenty years until Bernard et al (1978) described the distribution of C_1, C_2, $C_{2=}$, C_3, and $C_{3=}$ in shelf and slope sediment (< 2 m subbottom) of the Gulf of Mexico. Using similar headspace analysis techniques, Kvenvolden & Redden (1980) studied the occurrence and distribution of C_1, C_2, $C_{2=}$, C_3, $C_{3=}$, i-C_4, and *n*-C_4 in surface and near-surface sediment (< 2.5 m subbottom) of the outer shelf, slope, and basin of the Bering Sea. For headspace analyses, sediment samples are obtained using standard gravity or piston-coring techniques. Recovered cores typically are less than 5 m long, and extracted gas is analyzed by gas chromatography. The methods of headspace analysis provide a rapid quantitative measure of a portion of the gases originally in the sediment.

Headspace analyses of samples from the Gulf of Mexico (Bernard et al 1978) and the Bering Sea (Kvenvolden & Redden 1980) provide a measure of concentrations of hydrocarbon gases in near-surface, partially oxic sediments of open-marine environments of the shelf, slope, and basin. For example, typical background concentrations of C_1 in these sediments range from about 10^{-6} to 10^{-4} standard volumes of gas per volume of interstitial water (v/v). These concentrations are as much as three to five orders of magnitude lower than the concentrations of C_1 found at shallow (< 5 m) depths in some anoxic and low-sulfate sediments of restricted marine environments (Reeburgh 1969, 1976, 1980, Barnes & Goldberg 1976, Martens & Berner 1977, Kosiur & Warford 1979).

Generalizations also can be made about the occurrences of C_2 through C_4 hydrocarbons in sediments at shallow depth in open-marine environments. In the Gulf of Mexico and the Bering Sea, concentrations of C_2 are typically less than about 10^{-7} v/v, concentrations of C_3 are less than about 5×10^{-8} v/v, and concentrations of the sum of i-C_4 and *n*-C_4 are less than about 2.5×10^{-8} v/v. $C_{2=}$ and $C_{3=}$ concentrations are about the same order of magnitude as the concentrations of C_2 and C_3, with some variation depending on the environmental setting. Concentrations of C_2 through C_4 hydrocarbons do not appear to increase significantly with sediment depth within the uppermost 2 m; however, on a regional basis the average concentrations of C_2 through C_4 hydrocarbons do decrease with increasing depth of water from shelf to slope to basin.

Concentrations of C_2 through C_4 hydrocarbons may be much higher in sediments of restricted marine environments than in sediments of open-marine environments. For example, in sediments of Norton Sound, Alaska, concentrations of $C_2 + C_3$ reach about 2×10^{-6} v/v and of i-C_4 + *n*-C_4 about 2×10^{-7} v/v. However, C_1 in Norton Sound sediments reaches concentrations in excess of 2×10^{-2} standard volumes per volume of interstitial water at sediment depths of less than 3 m (Kvenvolden et al 1981a), so the concentration of C_{2+} hydrocarbons relative to C_1 actually can be less in restricted marine sediments, compared with open-marine sediments.

In considering the possible origin of hydrocarbons in near-surface, open-marine sediments, a comparison with hydrocarbons in seawater is instructive. Results of extensive studies of hydrocarbon gases in seawater have been summarized by Swinnerton & Lamontagne (1974). Table 2 shows that the hydrocarbon concentrations of near-surface marine sediment greatly exceed the average hydrocarbon concentration of open-ocean water. Thus, a water-column source for hydrocarbon gas in near-surface marine sediment is improbable.

Another possible explanation is that the hydrocarbon gases in the near-surface sediment of open-marine environments diffused or migrated upward from more deeply buried sediment. Although some movement from depth is certainly possible, the distribution of hydrocarbon gases in near-surface marine sediment, in general, does not provide compelling evidence for this source. Bernard (1979) concluded that upward diffusion from large accumulations of C_1 deeper than about 10 m would not be detectable in near-surface sediment. Profiles of concentrations of C_2 through C_4 hydrocarbons show little or no change with depth in near-surface sediments (Bernard et al 1978, Kvenvolden & Redden 1980). This kind of profile implies that the source of these hydrocarbons is probably not deeper in the sediment.

If the overlying water column and the underlying sediments are discounted as major sources of the hydrocarbons found in near-surface marine sediments, then these hydrocarbons must be generated in place. Microbial production (possibly in anoxic microenvironments) and consumption provide a reasonable explanation for the observed C_1 distributions in near-surface marine sediments of open-marine environments.

C_2, $C_{2=}$, C_3, and $C_{3=}$ hydrocarbons are known to be generated in connection with microbial processes (Davis & Squires 1954, Primrose & Dilworth 1976). Marine organisms produce both $C_{2=}$ and $C_{3=}$ (Hunt 1974), and studies of anoxic estuarine sediments indicate that small quantities of C_2 can be formed by certain methanogenic bacteria

Table 2 Concentrations of hydrocarbon gases in open-ocean water (Swinnerton & Lamontagne 1974) and near-surface sediment of open-marine environments (Bernard et al 1978, Kvenvolden & Redden 1980)

Gas	Open-ocean[a]	Near-surface sediment[a]
C_1	50	1000–100,000
C_2	0.5	20–100
$C_{2=}$	5	10–200
C_3	0.3	10–50
$C_{3=}$	1.4	5–100
C_4 (i-C_4 + n-C_4)	0.05	0–25

[a] Concentrations in 10^{-9} standard volumes of gas per volume of water (v/v).

(Oremland 1981). Prolonged incubation of these estuarine sediments also produce $C_{2=}$, C_3, $C_{3=}$, i-C_4, and *n*-C_4 (Vogel et al 1982). This kind of circumstantial evidence, combined with the common observation of small quantities of C_2 through C_4 hydrocarbons in recent marine sediments, has led some authors to suggest microbial processes as a reasonable source for these hydrocarbon gases (Emery & Hoggan 1958, Bernard et al 1978, Whelan et al 1980, Kvenvolden & Redden 1980).

Gases in Deeper Oceanic Sediment

Results obtained through the Deep Sea Drilling Project (DSDP) have provided an extensive record of hydrocarbon gases in deeper oceanic sediments, covering all of the oceans except the Arctic, and from sediment depths of a few meters to about 1500 m.

C_1 is the dominant hydrocarbon gas found in DSDP samples. Starting in about 1970 with DSDP Leg 10 in the Gulf of Mexico, gas samples have been collected routinely in evacuated containers (Gealy & Dubois 1971) or recovered from the headspace of sealed cans (McIver 1973) and analyzed by gas chromatography. Claypool et al (1973) summarize gas analyses of gas pockets in sediments collected on seven legs (10, 11, 13, 14, 15, 18 and 19) in the following areas: Gulf of Mexico, western Atlantic Ocean, Mediterranean Sea, Caribbean Sea, eastern and northern Pacific Ocean, and the Bering Sea. For all drilling sites except one, C_1 constituted more than 99.9 percent of the hydrocarbon gases detected. Utilizing gases in canned sediment samples, McIver (1975) showed that C_1 is virtually the only hydrocarbon gas present in 125 samples from 22 sites on eight DSDP legs (18, 19, 21, 23, 24, 27, 28, and 29) in the western and northern Pacific Ocean, Bering Sea, eastern Pacific Ocean, Arabian Sea, Red Sea, Gulf of Aden, Timor Sea, and the Antarctic Ocean. Thus the predominance of C_1 in marine sediments of the world's oceans is well established.

Although concentrations of C_2 are usually less than 0.1 percent of the hydrocarbon gases present in oceanic sediment, the ratio of C_2 to C_1 generally increases exponentially with depth in the sediment. This increasing ratio results mainly from increasing amounts of C_2 with depth, rather than from changes in the amounts of C_1. In Figure 3, the ratio of C_2 to C_1 is plotted as a function of depth of burial for a variety of depositional settings in the world's oceans, and the exponential increase in C_2 content with increasing depth is evident. At any given locality, the amount of C_2 appears to be proportional to the temperature and age of sediment (Rice & Claypool 1981).

Hydrocarbon gases larger than C_2, i.e. C_3, i-C_4, and *n*-C_4, also have been found in samples from DSDP drilling. $C_{2=}$ and $C_{3=}$ have not been reported. Routine detection and analysis of hydrocarbon gases larger than

C_2 required the application of a concentration technique to isolate the small amounts of the compounds usually present with C_1 from ocean sediment (Whelan 1979). Hunt & Whelan (1978) noted that C_1 was the dominant hydrocarbon gas in Black Sea sediment (Leg 42B), but that the gas mixture contained small amounts (10^{-6}–10^{-3} v/v) of C_2 through C_4 hydrocarbons. The concentrations of these hydrocarbons differed from each other by about an order of magnitude for each increasing carbon number; C_2 was most abundant. The trends of concentrations with depth for each of these hydrocarbons were similar.

Whelan (1979) observed trends of C_1 through C_4, as well as larger

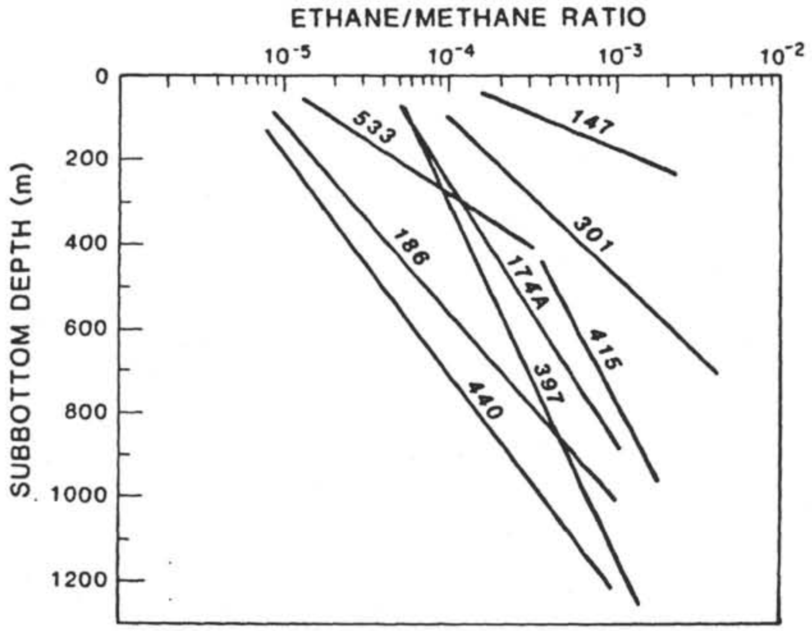

Figure 3 Ethane to methane ratios (C_2/C_1) vs depth in sediment from selected sites drilled by the Deep Sea Drilling Project.

Site	Leg	Location	Reference
147	15	Cariaco Trench, Caribbean	Rice & Claypool (1981)
174A	18	Astoria Fan, Pacific	Rice & Claypool (1981)
186	19	Aleutian Trench, Pacific	Rice & Claypool (1981)
397	47	African Margin, Atlantic	Whelan (1979)
415	50	Moroccan Basin, Atlantic	Galimov et al (1980)
440	57	Japan Trench, Pacific	Whelan & Sato (1980)
533	76	Blake Ridge, Atlantic	Kvenvolden & Barnard (1983a)

hydrocarbons, in continental margin sediments off northwest Africa that were similar to those observed for Black Sea sediments. Observations of C_2 through C_4 hydrocarbons in samples from DSDP drilling have now been augmented to include sediments from the Vigo Seamount (Whelan & Hunt 1979a), the Bay of Biscay (Whelan & Hunt 1979b), the Moroccan Basin (Galimov et al 1980, Whelan & Hunt 1980a), the Japan Trench (Whelan & Hunt 1980b), the California borderland (Whelan & Hunt 1981), and the Blake Outer Ridge (Kvenvolden & Barnard 1983a).

The C_2 through C_4 hydrocarbons accompaning C_1 in oceanic sediment probably have a complex history. They most likely represent products of a continuum of diagenetic processes, the first stages of which involve mainly microbiological processes operating near the sediment surface. These microbiological processes give way with sediment depth to processes that are thermally controlled at low temperatures. Thermal processes cause mild thermal decomposition of organic matter, resulting in the exponential increase with depth of C_2. Hydrocarbon gases C_3, i-C_4, and *n*-C_4 also tend, as a general rule, to increase slightly in concentration with depth. This increased concentration also may be attributed to low-temperature ($< 50°C$) thermal reactions. At temperatures existing in sediment at depths greater than those sampled by DSDP for gas analyses (i.e. greater than about 1500 m in regions with average thermal gradients), the thermal processes become more intense and result in the generation of gas associated with petroleum formation.

On the basis of all these observations, the following generalizations can be made: (*a*) C_1 is the most abundant hydrocarbon gas in deeper oceanic sediments, commonly constituting more than 99% of the hydrocarbon gas mixture; (*b*) C_2 through C_4 hydrocarbons are ubiquitous but minor components of the gas mixture in oceanic sediment; (*c*) C_2 generally increases exponentially in concentration with depth of sediment; and (*d*) the trends of C_2 through C_4 concentrations with depth are usually similar.

The isotopic composition of C_1 in the hydrocarbon gas mixtures in oceanic sediments provides the best evidence of origin (Rice & Claypool 1981). Table 3 shows the range of isotopic compositions of C_1 found in sediments drilled by DSDP. In most of the examples, the $\delta^{13}C$ values fall in a range between about $-90‰$ and $-50‰$. This range is characteristic of microbiologically derived C_1 from natural sources, as summarized by Fuex (1977). C_1 with carbon isotopic compositions more positive than about $-55‰$ in natural gas of near-surface sediment may result from partial microbial oxidative processes, as discussed by Silverman & Oyama (1968), Coleman et al (1981), and Barker & Fritz (1981). Carbon isotopic compositions of C_1 more positive than $-55‰$ also may be attributed to high-temperature thermal processes giving rise to C_1 that has migrated

Table 3 Carbon isotope composition of C_1 recovered through DSDP drilling of oceanic sediment

Location	DSDP Leg	$\delta^{13}C_1$ (‰)	Reference
Gulf of Mexico	10	−84.0 to −48.7	Claypool et al (1973)
East Mediterranean Sea	13	−77.8 to −72.6	Claypool et al (1973)
Caribbean Sea	15	−81.3 to −69.1	Claypool et al (1973)
Carioca Trench	15	−76.3 to −59.6	Lyon (1973)
Astoria Fan	18	−88.7 to −75.9	Claypool et al (1973)
East Aleutian Trench	18	−80.8 to −72.6	Claypool et al (1973)
Bering Sea, North Pacific	19	−78.8 to −62.7	Claypool et al (1973)
Arabian Sea	23	−82.8 to −61.0	Claypool (unpublished)
South Red Sea	23	−76.8 to −60.9	Claypool (unpublished)
Gulf of Aden	24	−76.2 to −70.2	Claypool (unpublished)
Timor Trench	27	−77.0 to −58.6	Claypool (unpublished)
Ross Sea	28	−78.9 to −67.5	Claypool (unpublished)
Sea of Japan	31	−72.0 to −67.4	Jodele & Doose (unpublished)
Norwegian Sea	38	−87.3 to −71.2	Morris (1976)
Black Sea	42A	−72.0 to −63.0	Hunt & Whelan (1978)
Continental Rise, NW Africa	41	−73.9 to −51.7	Doose et al (1978)
Continental Rise, NW Africa	47	−80.0 to −60.0	Whelan (1979)
Moroccan Basin	50	−82.1 to −49.2	Galimov et al (1980)
Japan Trench	56, 57	−83.8 to −67.6	Whelan & Sato (1980)
California Borderland, Baja	63	−81.6 to −47.3	Claypool (unpublished)
Gulf of California	64	−79.2 to −40.4	Galimov & Simoneit (1982)
Blake Outer Ridge	11	−88.4 to −70.1	Claypool et al (1973)
Blake Outer Ridge	76	−93.8 to −65.8	Galimov & Kvenvolden (1983)

from deeper sources (Fuex 1977). Measurement of the H/D ratio of C_1 can resolve these alternative interpretations based on $\delta^{13}C$, because partially oxidized C_1 is even more enriched in D than ^{13}C (Coleman et al 1981).

At many DSDP sites, profiles of C_1 isotopic values can be constructed with depth of burial (Claypool et al 1973, Claypool & Kaplan 1974, Doose et al 1978, Whelan 1979, Galimov et al 1980, Whelan & Sato 1980, Galimov & Kvenvolden 1983). These profiles consistently show the trends seen in Figure 2, and are believed to result from a kinetic effect of biological methanogenesis (Rosenfeld & Silverman 1959).

Except for a few instances, the molecular and isotopic compositions of hydrocarbon gases in oceanic sediments cannot be explained satisfactorily by upward migration of thermogenically derived gases. Such migration would require diffusion of gas through unconsolidated and semiconsolidated oceanic sediment. That sufficient diffusion could take place over the distance required is unlikely, even if the gas were present in large amounts at depth (Bernard 1979).

IMPLICATIONS OF HYDROCARBON GASES IN MARINE SEDIMENT

Geochemical Prospecting

Although the hydrocarbon gases in the first 1000 m of oceanic sediment beneath the seafloor can, in general, be accounted for by in situ processes, situations exist where gases originating elsewhere are associated with sediment. As explained earlier, hydrocarbon gases may be generated by nonbiologic processes in more deeply buried sediment, where temperatures exceed 80°C and petroleum is being formed. These gases, derived from the thermal breakdown of organic matter during later diagenesis, may migrate along fractures and faults to the seafloor. There, as gas seeps, they may provide clues to the presence of their petroleum precursors in the subsurface.

Active gas seeps in the marine environment are manifest as gas bubbles venting from the seafloor and as anomalously high concentrations of gas dissolved in the water column. Anomalous concentrations of hydrocarbon gases in the water column can be identified by analyses of gases (*a*) recovered as bubbles (Bernard et al 1976, Reed & Kaplan 1977), (*b*) extracted from discrete water samples (Brooks et al 1973, Cline & Holmes 1977), and (*c*) detected by gas sniffers (Sigalove & Pearlman 1975, Sackett 1977, Reitsema et al 1978).

Hydrocarbon gas compositions and $\delta^{13}C$ values of C_1, measured in bubbles from natural seeps and underwater vents from offshore production operations, provide the basis for distinguishing biogenic (microbially derived) from thermogenic (petroleum-derived) gas (Bernard et al 1976). Biogenic gas has $C_1/(C_2+C_3)$ ratios greater than 1000, which means that the mixture is almost exclusively C_1. The isotopic composition of this C_1 is lighter (more negative) than $-60^{\circ}/_{oo}$. Thermogenic gas has significant quantities of low-molecular-weight hydrocarbons, with $C_1/(C_2+C_3)$ ratios ranging from 0 to 50. The isotopic composition of thermogenic C_1 is usually heavier (more positive) than $-50^{\circ}/_{oo}$. Thus, the ratio $C_1/(C_2+C_3)$ and the isotopic composition of C_1 can, in concert, be used as diagnostic parameters to ascertain the source of hydrocarbon gases in natural seeps. Figure 4 shows the molecular and isotopic compositions of gases in seeps and vents. Whereas vent gases clearly have a thermogenic source, only one seep (#5 in Figure 4) in the Gulf of Mexico has that source. Of the remaining thirteen sampled seeps in the Gulf of Mexico, eight have biogenic sources and five apparently have mixed origins (Bernard et al 1976). At Coal Oil Point and Carpinteria, offshore southern California, the composition of gas bubbling from submarine seeps indicates a thermogenic source (Reed & Kaplan 1977).

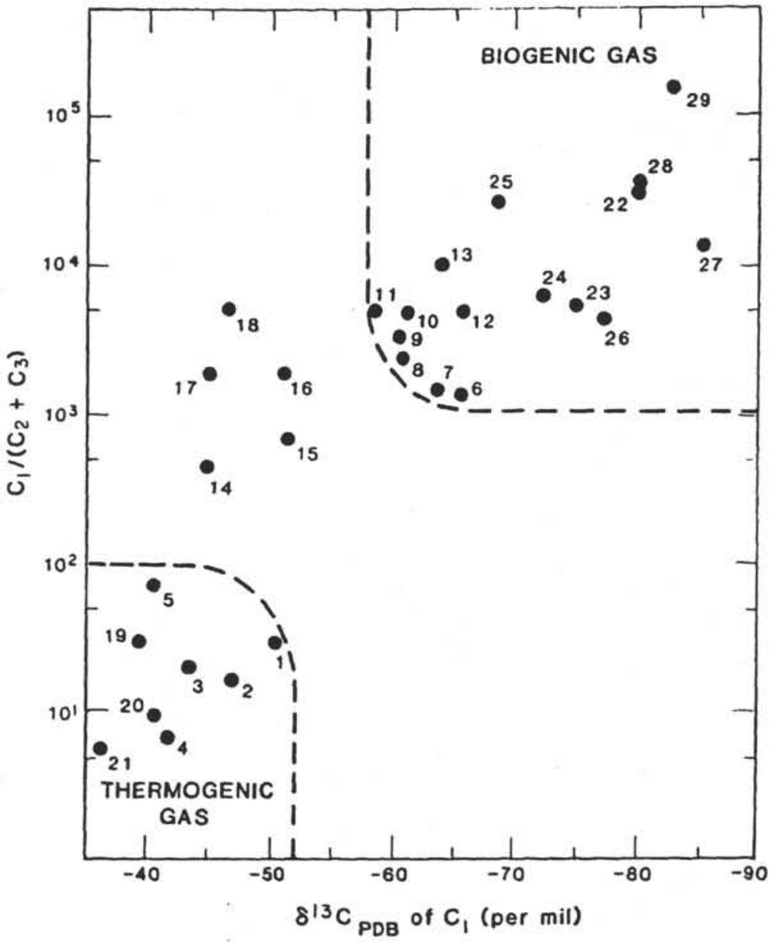

Figure 4 Relation between the logarithm of $C_1/(C_2+C_3)$ and the isotopic composition of C_1 for hydrocarbons in vents, seeps, and sediments.

Location	Numbers	Reference
Vents		
Gulf of Mexico	1–4	Bernard et al (1976)
Seeps		
Gulf of Mexico	5–18	Bernard et al (1976)
Offshore southern California	19–20	Reed & Kaplan (1977)
Norton Sound, Alaska	21–22	Kvenvolden et al (1979)
Norton Sound, Alaska	23–25	Kvenvolden et al (1981a)
Western Gulf of Alaska	26–29	Hampton & Kvenvolden (1981)

Before seeping into the water column, hydrocarbon gases may pass through unconsolidated surficial sediment at the seafloor. These hydrocarbons partially dissolve in the interstitial water and likely diffuse within the sediment. Therefore, in geochemical prospecting hydrocarbon gases in near-surface marine sediment might be examined for clues to the possible occurrence of petroleum at depth. Particularly informative results should be obtained from the analysis of sediments adjacent to active seeps. Carlisle et al (1975) examined sediments near an active seep and found a distinct hydrocarbon anomaly in which the $C_1/(C_2+C_3)$ ratio was less than 1, but no measurement was made of the isotopic composition of the C_1. In Norton Sound, Alaska, Kvenvolden et al (1979) measured the hydrocarbon gases in sediments associated with a CO_2 seep. A $C_1/(C_2+C_3)$ ratio of about 6 and a carbon isotopic composition of C_1 of $-36‰$ clearly indicate a thermogenic source of hydrocarbon gases (#21 in Figure 4). Even where active seepage is not present but where high concentrations of C_1 are present in sediment (exceeding about 10^{-3} standard volumes per volume of interstitial water), the molecular and isotopic gas compositions are diagnostic. For example, in Norton Sound (Kvenvolden et al 1981a) and the western Gulf of Alaska (Hampton & Kvenvolden 1981), the gas in near-surface, gas-charged sediment is from biogenic sources (Figure 4).

Although the $C_1/(C_2+C_3)$ ratio appears to be useful where gas concentrations are high, as in and near seeps and in gas-charged sediment, use of the ratio as an indicator of source is not yet clearly substantiated where low concentrations of hydrocarbon gases are dispersed within near-surface sediment (Kvenvolden & Redden 1980). Nevertheless, this ratio along with the ratio of $C_2/C_{2=}$ has been used to indicate the possible presence of thermogenic gas in near-surface sediment of St. George Basin in the southern Bering Sea (Kvenvolden et al 1981b), where two sites were identified with suspected thermogenic gas. This study also showed, however, that gas in surface grab samples has anomalously low $C_1/(C_2+C_3)$ ratios (less than 20). These low ratios probably do not signal the presence of thermogenic hydrocarbons, but rather indicate the preferential loss of C_1 owing to a balance between diffusion and selective microbial C_1 consumption.

Low concentrations of gas in near-surface sediment also limit the use of the isotopic composition of C_1 because the amount of C_1 collected usually is insufficient to obtain valid isotopic measurements. Where the carbon isotopic composition of C_1 can be determined for near-surface sediment, the C_1 may be anomalously heavy because the bacterial oxidation of C_1 leaves as a residual product an isotopically heavy C_1 (Coleman et al 1981). Thus, the $C_1/(C_2+C_3)$ ratios and the carbon isotopic compositions of C_1 in gases from near-surface sediment may have values that are characteristic of thermogenic sources, but the gases themselves may be the product of in situ processes strongly mediated by microbial activity. Application of these parameters as source indicators to the gases found in near-surface sediments is therefore limited, especially where low gas concentrations occur. Deeper sampling (to depths greater than about 2 m) may provide samples of gas that are not significantly affected by near-surface processes and thus are of potential use in geochemical prospecting for hydrocarbons.

Gas Hydrates

In general, solubilities of hydrocarbon gases in the interstitial waters of oceanic sediment increase with increasing depth of burial, but details regarding solubility have been worked out only for C_1 [see Rice & Claypool (1981) for a discussion]. Figure 5 shows the estimated solubility of C_1 as a function of depth. C_1 solubility increases with increasing depth of burial beneath water depths less than 1000 m. However, for deep-sea sediments at water depths greater than 1000 m, solubility initially decreases between sediment depths of 1000 and 2000 m before increasing at greater burial depths. Where water is saturated with C_1 at the depths indicated on Figure 5, the water can crystallize as a solid at temperatures above 0°C by the incorporation of C_1 into a clathrate, or three-dimensional framework of water molecules, that is stabilized by the included C_1 molecules. This water clathrate is commonly called a *gas hydrate.*

In gas hydrates, water crystallizes in the isometric system, rather than in the hexagonal system of normal ice. The isometric or cubic lattice contains voids, or cages, large enough to accommodate molecules of gas. Two structures of the cubic lattice are possible. In structure I, the cages are arranged in body-centered packing and include small hydrocarbon molecules such as C_1 and C_2 and nonhydrocarbons such as N_2, CO_2, and H_2S. In structure II, diamond packing is present; not only can C_1 and C_2 be included in the cages, but C_3 and i-C_4 also are needed to occupy some of the large cages in order to stabilize the structure. Apparently, gas molecules larger than i-C_4—for example, *n*-C_4, C_5's, etc—cannot be included in either structure I or II (Hand et al 1974, Hitchon 1974).

The pressure (depth)-temperature region in which pure C_1 forms a gas hydrate with pure water saturated with C_1 is shown in Figure 6. Gas extracted from oceanic sediment, however, is not pure C_1; it also has small concentrations of C_2 and hydrocarbon gases of higher molecular weight as well as CO_2. The presence of these additional components in the gas mixture causes the phase boundary (Figure 6) to shift to the right. Porewater in normal oceanic sediment is not pure but contains salts, particularly NaCl. The presence of salts in the water shifts the phase boundary to the left (Figure 6). For naturally occurring gases in oceanic

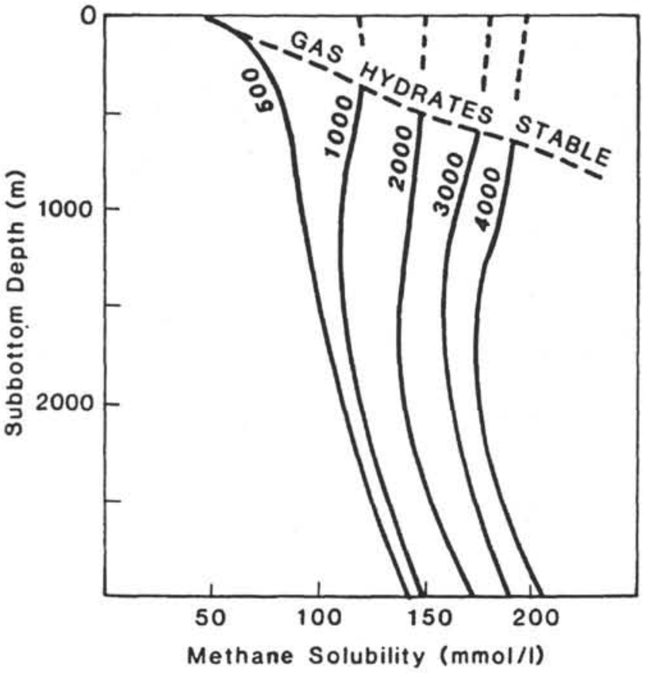

Figure 5 Estimated methane (C_1) solubility with depth of burial in oceanic sediment. The relation between C_1 solubility and the depth at which gas hydrates are stable is shown. Curves are for specific water depths (labeled in meters). The solubility data are from Culberson & McKetta (1951) and have been reduced 80% of the observed solubility of C_1 in pure water at a given temperature and depth to adjust for effects of 3.5‰ salinity. The series of curves indicate the changes of solubility at different pressure-temperature gradients associated with water depths from 0 to 4000 m. The pressure gradient is assumed to be hydrostatic (0.1 atm m^{-1}) and a geothermal gradient of 35°C km^{-1} is used. The temperature of sediment with no burial is assumed to be 20°C for a water depth of 0 m, 5°C for water depths of 500 m, and 2°C for water depths of 1000 m and greater. Figure is redrawn from Rice & Claypool (1981).

sediment, the shifts in the position of the phase boundary are of similar magnitude but in opposite directions. Thus, the effects approximately cancel each other, and the boundary for a pure-water and pure-methane system (Figure 6) provides a reasonable estimate of the pressure-temperature conditions under which natural gas hydrates, composed mainly of C_1, will be stable in oceanic sediment (Claypool & Kaplan 1974).

Because pressure is largely determined by water depth, the temperature established by the geothermal gradient mainly controls the lower depth limits within oceanic sediment at which gas hydrates are no longer stable and therefore decompose. The base of the gas hydrate zone follows a pressure-temperature surface that represents the maximum depth at which

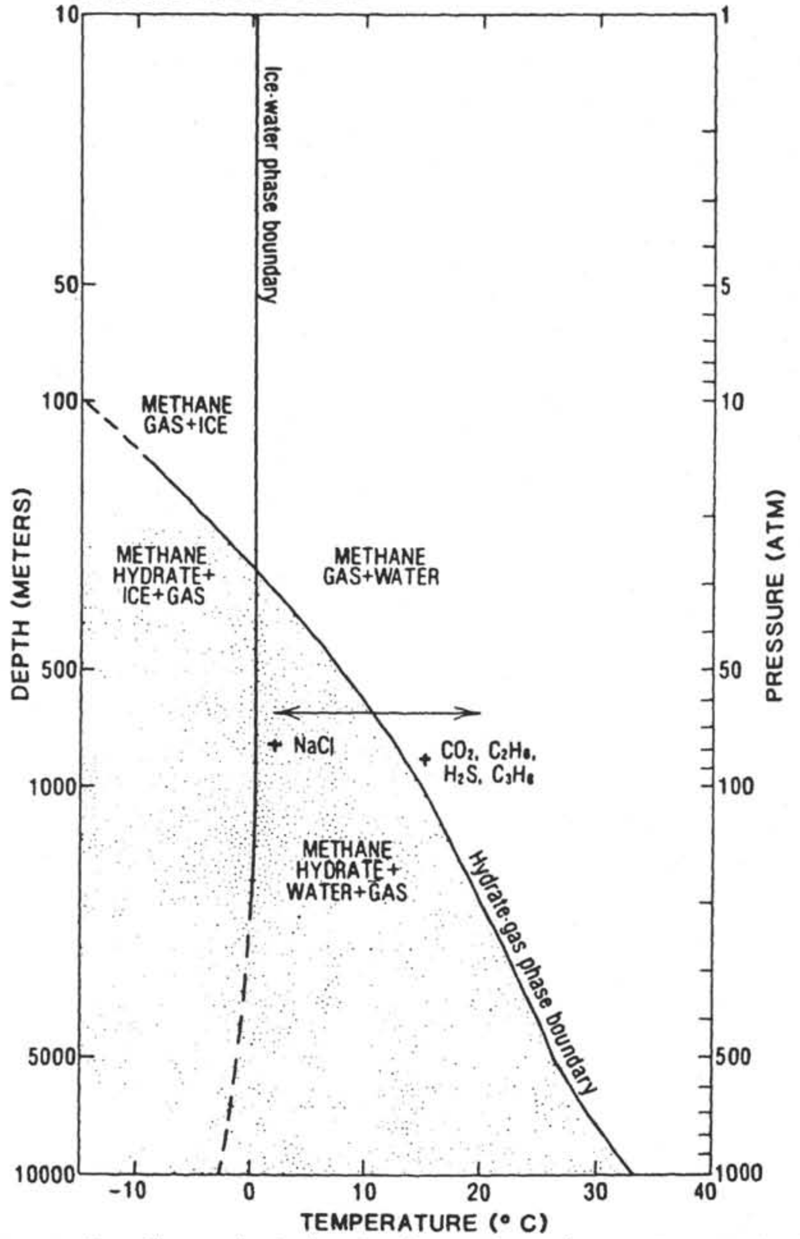

Figure 6 Phase diagram showing boundary between free methane gas (no pattern) and methane hydrate (pattern) for a pure-water and pure-methane system. Addition of NaCl to water shifts the curve to the left. Addition of CO_2, H_2S, C_2, and C_3 shifts the boundary to the right, thus increasing the area of the gas hydrate stability field. Depth scale assumes lithostatic and hydrostatic pressure gradients of 0.1 atm m^{-1}. Figure was constructed from Katz et al (1959) and redrawn from Kvenvolden & McMenamin (1980).

the gas hydrate is stable. Therefore, beneath the gas hydrate zone free gas may be present in gas-saturated sediments.

The base of the gas hydrate zone often correlates with anomalous acoustic reflectors in marine seismic data obtained from a number of areas on outer continental margins (Shipley et al 1979). The anomalous reflector approximately parallels the seafloor but deepens with increasing water depths. The depths at which this reflector occurs can be predicted based on considerations of the pressure-temperature stability field for gas hydrates and the geothermal gradient. The reflector commonly is called a *bottom-simulating reflector* (BSR). The BSR probably results from the velocity contrast between sediment cemented with gas hydrate and underlying sediment in which lower velocities occur because of the absence of gas hydrate and the possible presence of free gas.

Kvenvolden & McMenamin (1980) and Kvenvolden & Barnard (1983b) have summarized the geologic occurrences of natural gas hydrates and listed areas where the presence of marine gas hydrates can be inferred based on observations of BSRs on marine seismic records. Marine gas hydrates can be found in continental margin sediment of all the world's oceans. In spite of the apparent ubiquity of gas hydrates in continental margin sediment, solid samples of gas hydrate have been recovered from oceanic sediment in only three areas—the Black Sea in Russia (Yefremova & Zhizhchenko 1975), the Blake Outer Ridge in the Atlantic Ocean offshore from southern United States (Sheridan et al 1982), and the landward flank of the Middle America Trench in the Pacific Ocean offshore from Central America (Moore et al 1979, von Huene et al 1980, Aubouin et al 1982). Gas from these samples was mainly C_1 accompanied by minor amounts of the heavier hydrocarbon gases. The carbon isotopic composition of C_1 from sediments recovered from the Black Sea (Hunt & Whelan 1978) and from the Blake Outer Ridge (Claypool et al 1973, Galimov & Kvenvolden 1983) range from $-63^{\circ}/_{\circ\circ}$ to $-94^{\circ}/_{\circ\circ}$. These values fall in the range (-50 to $-90^{\circ}/_{\circ\circ}$) that is generally considered to indicate biogenic C_1. Thus, the C_1 in marine gas hydrates in these two areas likely results from the bacterial alteration of organic matter buried in the sediment.

Preliminary unpublished results of measurements of the molecular and isotopic compositions of gas from a massive gas hydrate recovered in sediments at one site from the Middle America Trench (DSDP Leg 84) indicate a possible thermogenic source for C_1 ($\delta^{13}C = -41^{\circ}/_{\circ\circ}$). However, this C_1 occurs with extremely ^{12}C-depleted $\sum CO_2$ ($+37^{\circ}/_{\circ\circ}$) and thus alternatively could be an unusual example of isotopically heavy biogenic C_1. Electric logging showed that the massive hydrate is about 3 m thick at a sediment depth of 250 m. The gas hydrate at this site apparently made room for itself during the crystal-forming process, resulting in a massive gas hydrate containing minor quantities of sediment.

Gas hydrates may act as a seal, trapping C_1 and other hydrocarbon gases beneath them (Hedberg 1980, Dillon et al 1980). If the interface between the base of the gas hydrate and the region of free gas intercepts porous and permeable beds, situations may be created where gas hydrates trap free gas in economically producible reservoirs. However, evidence for the widespread occurrence of such reservoirs associated with marine gas hydrates has not yet been clearly documented.

CONCLUSIONS

Hydrocarbon natural gas in oceanic sediment has multiple mechanisms of origin, although the most important one is C_1 generation by microbiological decomposition of organic matter. Profiles of $\delta^{13}C_1$, $\delta^{13}C$ of $\sum CO_2$, and C_2/C_1 ratios in the intermediate subbottom depth range (50–1000 m) indicate that microbiological C_1 generation is widespread in anoxic, sulfate-depleted ocean sediments. C_1 of thermogenic origin (along with C_2, etc) becomes a more important component of the gas mixture with increasing depth of burial. Thermogenic gas can be a major component locally where gas of a deeper, high-temperature ($> 100°C$) origin migrates to shallower marine sediments. In oxidizing marine sediments at relatively shallow depths (< 10 m) beneath the seafloor, the small amounts and variable composition of hydrocarbon gas are determined by both generation and consumption processes.

Attempts to locate buried petroleum accumulations in marine sediments by detecting gas seeps on the seafloor must take into account the effects on gas composition of both the mechanisms of origin and near-surface alteration. Where hydrocarbon gas occurs in concentrations sufficient to saturate the interstitial water of marine sediment, either a free gas phase will form or the gas in excess of porewater solubility will form solid gas hydrate, depending on pressure and temperature. Gas hydrates composed largely of microbiological C_1 appear to be widespread in marine sediments near continental margins, but gas of deeper origin also may contribute to gas hydrate formation in some circumstances.

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APPENDIX D

Hydrates of Natural Gas: A Review of Their Geologic Occurrence

By Keith A. Kvenvolden and Mark A. McMenamin

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Hydrates of Natural Gas:
A Review of Their Geologic Occurrence

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SUMMARY

Gas hydrates are a type of inclusion compound or clathrate formed as icelike mixtures of gas and water in which gas molecules are trapped within a framework or cage of water molecules. Large quantities of natural gas (mainly methane) can be trapped in sediments in the form of gas hydrates. The pressure and temperature conditions for the formation of gas hydrates are found in regions of permafrost and beneath the sea in outer continental margins and ocean basins. In addition to suitable temperature and pressure conditions, sufficient concentrations of methane must be present for hydrate stability. This methane may be produced in sediments by biological processes; however, the extent of this production is not fully understood. Methane could also migrate from thermochemically altered organic matter at depth.

The presence of gas hydrates in permafrost regions has been established at the Messoyakha gas field in western Siberia, in two exploratory wells in the Mackenzie Delta area of Canada, and in a wildcat well on the North Slope of Alaska. In the Alaskan well, a pressure core barrel successfully recovered gas hydrate in sediment at in situ temperature and pressure. Although gas hydrates have now been identified in permafrost areas, the geographical extent of these hydrates has not yet been determined.

Geologic, geochemical, and geophysical evidence suggests that gas hydrates can exist in many areas beneath the seafloor. Geologic evidence consists of (1) widespread areas where pressures and temperatures are suitable for gas-hydrate stability and (2) recovery of deep-sea sediment cores that release gas and cool endothermically when exposed to sea-level temperature and pressure. Geochemical observations include (1) high concentrations of methane in sediment, usually accompanied by low concentrations of ethane, and (2) gas released from thawing cores in the volumes expected for the decomposition of gas hydrate. Geophysical evidence includes (1) seismic anomalies that can be explained by the properties of sediments containing hydrates, (2) high acoustic velocity in sediments from suspected hydrate zones, and (3) laboratory experiments which show that the acoustic velocities of sediment increase when gas hydrate is formed in the sediment.

The main seismic evidence for submarine gas hydrates are reflectors that simulate the topography of the seafloor. Such reflectors appear on seismic records from the east coast of North America, the North Pacific, the Bering Sea, and the Pacific and Atlantic coasts of Central America. They lie anywhere from 100 to 1,100 meters below the bottom. Bottom-simulating reflectors have been seen only in water deeper than 400 m and are generally manifest on seismic records as a reflection polarity reversal caused by an abrupt decrease in seismic velocity. The exact relations of bottom-simulating reflectors to gas hydrate zones are uncertain. The change in seismic impedance may mark the bottom of the gas-hydrate zone where free methane gas is trapped beneath the hydrate layer. Other features on seismic records that may indicate the presence of hydrates are bottom-paralleling bright spots, pagoda structures, and deep-water velocity amplitude features (VAMP's).

Not all bottom-simulating reflectors may be directly related to gas hydrates. For example, a bottom-simulating reflector lacking polarity reversal in sediments of the Bering Sea is currently thought to represent a migrating diagenetic boundary related to the dissolution of diatoms and the induration of claystone.

If large quantities of gas hydrate are widespread in permafrost regions and in offshore marine sediments, they may be potential energy resources. The gas within the hydrate itself may

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not be recoverable, but the free gas trapped beneath it may be the important resource.

INTRODUCTION

Gas hydrates are a special kind of clathrate formed from a mixture of natural gas and water. Clathrates are inclusion compounds in which two or more chemical compounds form a stable crystalline mixture. One constituent forms the clathrate framework, a molecular lattice with an ordered geometric pattern. The other constituents of the clathrate fill the sites or cages within the framework structure. A clathrate framework, because it may contain many vacant sites, is a nonstoichiometric substance (a substance that cannot be accurately described by a single chemical formula). Water, because of its hydrogen-bonding properties, is an excellent clathrate framework compound. An expanded ice lattice forms cages that can contain gas molecules such as argon, methane, propane, isobutane, sulfur dioxide, carbon dioxide, and hydrogen sulfide.

The term "gas hydrate" is used here to mean a water-methane clathrate that may or may not contain ethane, propane, and other hydrocarbons. Under suitable pressures, natural gas, which contains mainly methane, can interact with water to form a solid icelike mixture, that is, a gas hydrate, at temperatures considerably above the freezing point of water (fig. 1). The amount of methane needed for hydrate formation depends on temperature and pressure. In the methane-water system, only methane present in excess of the amount soluble in water is available for hydrate formation. In an ideally saturated hydrate, with all cages filled by methane molecules, the molar ratio of methane to water can be nearly 1:6. The formula for an ideal stoichiometric methane-water clathrate is $CH_4 \cdot 5\text{-}3/4H_2O$. One cubic meter of this ideal hydrate would contain the equivalent of about 170 cubic meters of free methane gas. Gas hydrates found in nature contain less gas than this because the lattice cages are not completely filled. Nevertheless, gas hydrates in reservoir rocks can contain much more methane per unit volume than could be contained as free gas in the same space. This fact suggests that if gas hydrates exist in large quantities in the upper few hundred meters of the earth's crust, they would constitute a significant potential energy resource. Also, because gas hydrates are impermeable to free gas, a layer of hydrate could trap economically important quantities of free gas below it.

Petroleum exploration drilling in Arctic regions has established the occurrence of gas hydrate below permafrost (fig. 2). Marine seismic studies and Deep Sea Drilling Project cores strongly indicate the presence of gas hydrates in some seafloor sediments (fig. 2). This paper reviews what is known about these naturally occurring gas hydrates.

GAS HYDRATES IN PERMAFROST REGIONS

The fact that temperature and pressure conditions beneath permafrost regions fall within the stability field of gas hydrates (fig. 3) was recognized in the 1940's. Now several deposits of gas hydrate are known (table 1). In 1970, well logging and formation tests in the Messoyakha gas field in western Siberia revealed billions of cubic meters of methane gas frozen as gas hydrate (Makogon and others, 1971, 1972; both

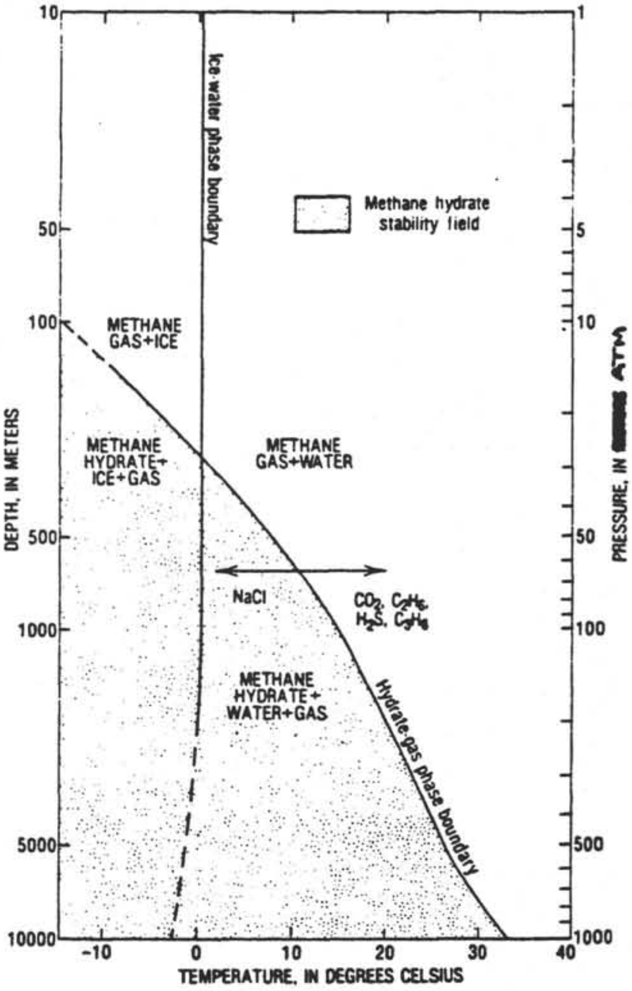

Figure 1—Phase boundary diagram showing free methane gas and methane hydrate (pattern) for a fresh water-pure methane system. Addition of NaCl to water lowers temperature of hydrate formation, in effect shifting gas-hydrate curve to left. Addition of CO_2, H_2S, C_2H_6, or C_3H_8 raises temperature of hydrate formation, in effect shifting curve to right. Therefore, impurities in natural gas will increase area of hydrate stability field. Depth scale is an approximation assuming that lithostatic and hydrostatic pressure gradients are both 0.1 atmosphere per meter (10.1 kPa/m), but the true lithostatic gradient is slightly greater. Redrawn after Katz and others (1959).

Figure 2.--Known and inferred accumulations of gas hydrate. Dots on land depict suspected or confirmed occurrences of gas hydrates beneath permafrost. Dots in oceans show areas where seismic or drilling evidence suggests presence of gas hydrates. See tables 1 and 2 for a listing of each site, along with geologic, geophysical, and geochemical evidence for hydrate presence, research organization involved, and pertinent references.

references cited by Milton, 1976). Methane was released from the gas hydrate by injecting methanol into test wells that perforated the hydrate zone. The injections of methanol, which serves as a hydrate inhibitor, resulted in a large increase in gas productivity from the test wells. The parts of the Messoyakha field containing gas hydrates are calculated to have 54 percent more reserves than would be expected in an equal volume of reservoir rocks filled with free gas.

Two exploratory wells drilled in permafrost of the Mackenzie Delta penetrated shallow sand reservoirs containing gas hydrate at depths of 820 to 1,100 m (Bily and Dick, 1974). The amount of formation gas in the drilling mud increased significantly during penetration of these sands. Although these sands were very porous, their permeability was extremely low. Low permeability and pronounced gas release are characteristic of hydrate-filled reservoirs. The low permeability is thought to result from the plugging of sediment interstices by gas hydrate, and the gas liberated is attributed to hydrate decomposition.

Other characteristics of the gas hydrate zone are visible on well logs (Bily and Dick, 1974). The hydrate-bearing sands have a relatively high resistivity. Spontaneous potential (SP) curves show very little deflection in hydrate zones in comparison with deflections in free-gas and free-water zones. Sonic logs show

Table 1.--Evidence for gas hydrates beneath permafrost

Number on fig. 2	Location	Permafrost thickness (m)	Predicted depth range of hydrate (m)	Geophysical evidence	Geochemical evidence	Research organization	References
1	Messoyakha gas field and northwestern Siberia, U.S.S.R.	450	250-870		90 pct. or more methane in gas analysis; large volume of gas from thawed cores.	U.S.S.R.	Makogon and others, 1971.
2	Mackenzie Delta, Northwest Territories, Canada	610	820-1100	Well logs: small deflection in SP; high resistivity; high velocity sonic log; over-gage caliper log.	do.	Imperial Oil, Ltd.	Bily and Dick, 1974.
3	West Prudhoe Bay, Alaska, U.S.A.	610	210-1100	Well logs: high resistivities; high velocity sonic log; gas kicks in mud logs.	do.	Exxon	R. D. McIver, written commun., 1979.
4	Arctic Archipelago, Northwest Territories, Canada	530	No data in print.		No data in print	Dome Petroleum, Ltd.	Hitchson, 1974.
5	Vilyuy Basin, Yakutia, U.S.S.R.	>500	do.		do.	U.S.S.R.	Makogon and others, 1972.

an increase in acoustic velocity, and the caliper log indicates over-gage borehole through many hydrate-bearing zones.

The first conclusive confirmation that gas hydrates occur in sediments under permafrost was obtained from pressure core barrel samples at the Arco-Exxon N.W. Eileen State No. 2 wildcat well on the north slope of Alaska in the West Prudhoe Bay field (R.D. McIver, written commun., 1979). Two pressurized cores were successfully recovered and were maintained in the barrel at temperatures slightly above 0°C. At the time the cores were collected it was uncertain whether the cores had contained gas hydrate or only pressurized free methane. If the cores had contained free gas at in situ temperature and pressure, the pressure in the barrel would have been expected to decrease linearly as gas was withdrawn from the barrel. However, pressure was maintained even after repeated samples were withdrawn. This result could only have been caused by the decomposition of hydrate after each increment of pressure release and gas removal. Immediately after each sample was removed and the system closed, pressure began to build toward the pressure of hydrate equilibrium. The sampled gas was 93 percent methane and 7 percent nitrogen.

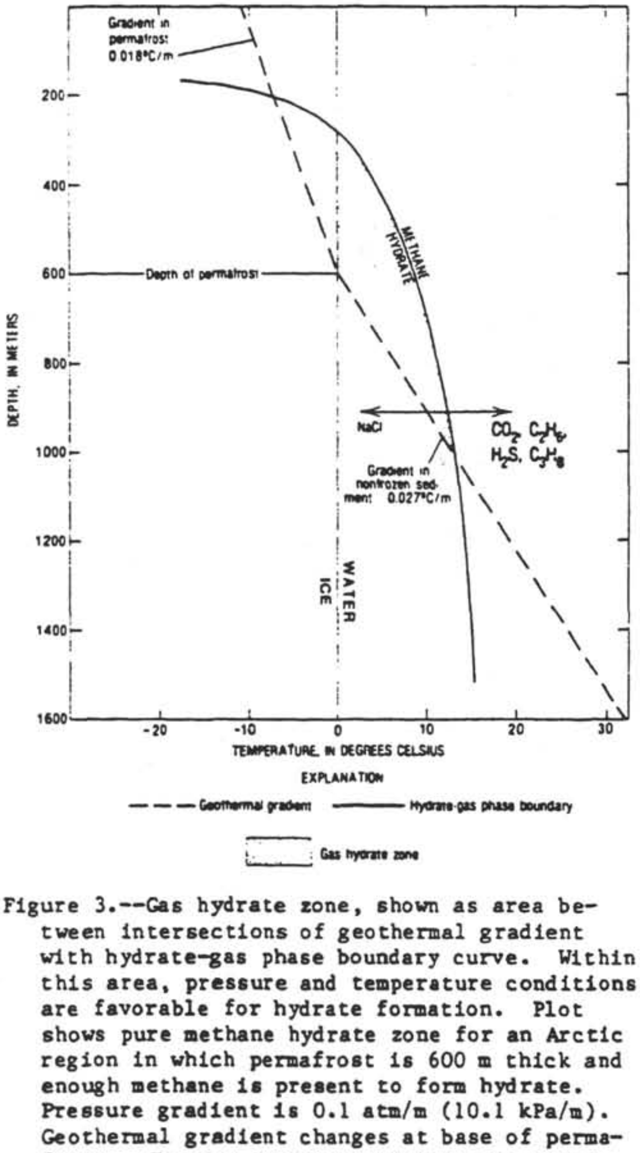

Figure 3.--Gas hydrate zone, shown as area between intersections of geothermal gradient with hydrate-gas phase boundary curve. Within this area, pressure and temperature conditions are favorable for hydrate formation. Plot shows pure methane hydrate zone for an Arctic region in which permafrost is 600 m thick and enough methane is present to form hydrate. Pressure gradient is 0.1 atm/m (10.1 kPa/m). Geothermal gradient changes at base of permafrost. Changes in gas composition or water salinity will shift phase boundary curve in same sense as figure 1. Redrawn after Bily and Dick (1974).

Well logs in the Eileen well also indicated the hydrate zone. Whereas strong mud-gas shows suggested free gas in the formation, the high resistivities and high velocities on the sonic log indicated ice or icelike materials. The density log also responded as if there were ice rather than gas in the formation. In combination the resistivity, sonic, and mud logs pointed to the presence of hydrates.

In addition to the North Slope, the Mackenzie Delta, and the western Siberian basin, the Arctic Archipelago of Canada and the Vilyuy basin of the U.S.S.R. show evidence of gas hydrate deposits. Gas-flow data from a well in Winter Harbor in the Arctic Archipelago suggested the presence of gas hydrates (Hitchon, 1974). Makogon and others (1972) reported that the Central Vilyuy gas field in Yakutia, U.S.S.R., contains gas hydrates beneath permafrost.

Any sedimentary basin with extensive areas of relatively thick (several hundred meters) continuous permafrost may contain potentially commercial occurrences of gas hydrates. Antarctica may have large gas hydrate accumulations, although few data on Antarctic permafrost areas are available (Hitchon, 1974). No drilling program has been conducted on the Antarctic continent except for a few experimental holes, but the land temperature profile is such that gas hydrates could exist at depths of more than 1,800 m.

GAS HYDRATES IN OCEANIC SEDIMENTS

Pressure and temperature conditions in the deep sea floor are within the range of gas hydrate stability (fig. 4), and the possible presence of gas hydrates has been noted in several areas (table 2). Observation of deep-sea sediment cores that release large quantities of methane suggest that gas hydrates exist in some areas beneath the seafloor. In reviews of sediment gas data from the Deep Sea Drilling Project (DSDP), Claypool and others (1973; Legs 10-19) and McIver (1974; Legs 18-23) described instances where gas evolved from core samples after they were taken on deck. Gas evolution sometimes continued for several hours, and the pressures generated were occasionally sufficient to extrude cores from the barrel and rupture sealed containers. The expanding, cooling gas formed ice on the exposed cores. The quantity and rate of gas evolution could indicate the decomposition of gas hydrate, although high concentrations of gas not in hydrated form can produce similar results. In most instances, the gas was methane with traces of ethane. Recent results from DSDP Legs 66 and 67 provide more evidence for the presence of gas hydrates in sediments on the slope of the Mid-America Trench off Central America (Geotimes, 1979a, 1979b). On both of these legs, gas-releasing cores were observed. Frozen sediment was recovered from the zone of hydrate stability at Sites 490, 491, 492, 497, and 498. Gas expansion volumes as high as 50 to 1 (R. von Huene, oral commun., 1979) suggest that gas hydrates had indeed been sampled.

Methane in ocean sediment may be of either biochemical or thermal origin. It is uncertain, however, that enough gas to support the formation of gas hydrate can be generated by methane-producing bacteria alone. Claypool and Kaplan (1974) estimated that biological generation of methane in sediment containing 0.5 percent organic carbon near sediment depths of around 1,000 m (corresponding to 30°C) is 20 mmol per kilogram of interstitial water. They also estimated the threshold methane concentration for hydrate stability as 58 mmol/kg. Thermocatalytic methane is produced by alteration of organic matter at temperatures greater than 50°C, but gas hydrates are stable only at relatively low temperatures. For gas hydrates to form from thermocatalytic natural gas (methane), such gas must migrate upward from burial depths greater than 1,500 m into cooler regions where it could be incorporated into a gas hydrate zone.

BOTTOM-SIMULATING REFLECTORS

A bottom-simulating reflector is an anomalous seismic reflector that parallels the topography of the seafloor but lies anywhere from 100 to 1,100 m below the bottom. Bottom-simulating reflectors are most easily recognized on seismic records when they cut across other reflectors and occur in water depths greater than 400 m. They

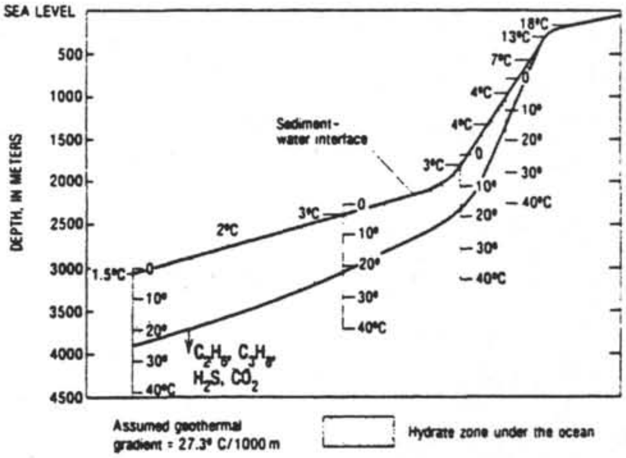

Figure 4.—Idealized section of gas hydrate zone in sediments of outer continental margins, computed for pure methane. Stippled zone is potential area of hydrate formation, where pressure and temperature conditions are correct for hydrate stability assuming an adequate supply of methane. Presence of other gases in methane would increase methane hydrate envelope downward. Increasing pressure from height of water column causes increase in subbottom depth of gas hydrate zone. Decreasing sediment temperature (down to 1°C in coldest, deepest bottom waters) also [illegible]creases hydrate subbottom depth. Redrawn from R.D. McIver, written commun., 1979.

Table 2.—Evidence for gas hydrates in the seafloor

Number on fig. 2	Location	Water depth (m)	Predicted subbottom depth range of hydrate (m)	Bottom-simulating reflectors (subbottom depth, m)	Other geophysical evidence	Geochemical evidence	Research organization	References
6	Blake-Bahama Outer Ridge, western Atlantic, off east coast of U.S.A.	3700	0-1000	about 500		90 pct. or more methane in gas analysis; large volume of gas from thawed cores.	Lamont-Doherty, DSDP, and USGS.	Markl and others, 1970; Ewing and Hollister, 1972; Dillon and others, 1980.
7	Bering Sea, North Pacific	2000-4000+	0->1000	580-670	VAMP's, >500 m beneath the seafloor.	90 pct. or more methane in gas analysis.	DSDP and USGS	Scholl and Creager, 1973; Scholl and Cooper, 1978.
8	Beaufort Sea, Arctic Ocean	400-2500+	0-700+	100-300		No data in print	USGS	Grantz and others, 1976.
9	Western North Atlantic	2500-3800	0->1000	500-600		do.	Lamont-Doherty	Tucholke and others, 197’.
10	Western Gulf of Mexico	1200-2000	0-500	100-1100		do.	Univ. of Texas, Marine Science Institute.	Shipley and others, 1979.
11	Northern Colombian and northern Panamanian coasts	1500-3000	0-800	100-1100		do.	do.	Do.
12	Central America, Pacific side	800-2400	0-650	100-1100		do.	do.	Do.
13	Western Africa	2000-5500	0->1000		Pagoda structures at very shallow depth.	do.	Woods Hole, Mass.	Emery, 1974.
14	Gulf of Oman	3000	0-800		Bright spots at 600-700 m depth.	do.	Cambridge, U.K.	White, 1979.

are generally characterized by reflection polarity reversals and large reflection coefficients (Shipley and others, 1979). Gas hydrate zones and diagenetic boundaries in sediment have been proposed as possible causes of these anomalous seismic reflectors.

Before DSDP Leg 11 in the Blake-Bahama region of the Atlantic Ocean, geophysicists of the Lamont-Doherty Geological Observatory were intrigued by bottom-simulating reflectors on their seismic records over the Blake-Bahama Outer Ridge (Markl and others, 1970; Stoll and others, 1971). The observation that some of the seismic reflectors on their records intersected other reflectors and paralleled the seafloor (fig. 5) was unexplained. One of the major objectives of Leg 11 was to investigate the nature of the bottom-simulating reflectors and determine their relation, if any, to accumulations of gas hydrate beneath the seafloor. The strongest reflector on the ridge mimicked the ridge profile at a depth of more than 500 m below the seafloor. Samples from Sites 102, 103, and 104 of Leg 11 yielded mainly methane and traces of ethane (for quantitative gas composition data see Claypool and others, 1973). The strong bottom-simulating reflector was at that time correlated with a distinct break in the drilling rate and with a zone of nodules of siderite and ankerite (Lancelot and Ewing, 1972). Another explanation, suggested by Stoll, Ewing, and Bryan (1971), Ewing and Hollister (1972), and Dillon, Grow, and Paull (1980), is that the bottom-simulating reflector corresponds to the isotherm that separates a gas environment from a gas hydrate environment. The average thermal gradient for the ridge (about 35-40°C/km) permits a gas hydrate to exist at the 500-m sediment depth of the strong reflector, but below that level the temperature would be high enough that methane could exist only as a gas. The interface between gas hydrate above and free gas below could provide a velocity contrast that is responsible for the bottom-simulating reflector. Furthermore, the apparent acoustic velocity through sediment overlying this reflector was determined to be about 2 km/s (Lancelot and Ewing, 1972). This value, later confirmed by independent sonobuoy measurements (Bryan, 1974), is unusually high for hemipelagic sediment.

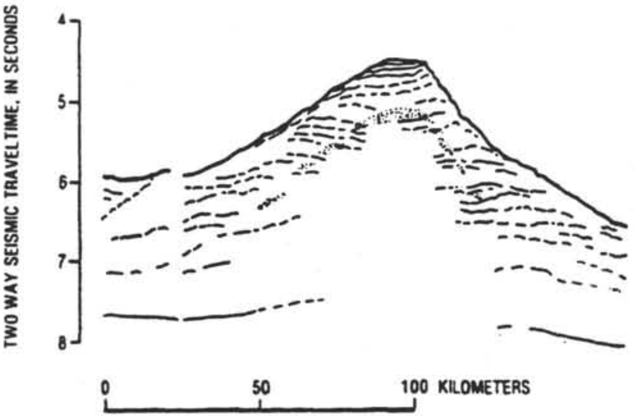

Figure 5.--Diagrammatic seismic profile of Blake-Bahama Outer Ridge, showing thin, regularly spaced reflectors from strata. Bottom-simulating reflector (stippled) transects bedding and parallels seafloor and may represent hydrate-to-free-gas transition at bottom of gas hydrate zone. Redrawn from Tucholke and others (1977).

Laboratory experimental studies provide further evidence linking gas hydrates with the sediments of the Blake-Bahama Ridge. Stoll, Ewing, and Bryan (1971) demonstrated that when methane mixed with water-saturated sand was brought to the estimated temperatures and pressures of the Blake-Bahama Ridge sediment, the velocity of compressional seismic waves in the sand increased from 1.7 to 2.5 km/s. This experimental increase in seismic velocity helps explain the unusually high velocities observed in hemipelagic sediment of the ridge.

Since they were first found in the Blake-Bahama Ridge (Markl and others, 1970; Ewing and Hollister, 1972), other bottom-simulating reflectors have been reported (fig. 3) from the western North Atlantic Ocean (Tucholke and others, 1977), the Beaufort Sea of the Arctic Ocean (Grantz and others, 1976), and the Bering Sea and elsewhere in the North Pacific Ocean (Scholl and Creager, 1973). Shipley and others (1979) described bottom-simulating reflectors in sediments off the east coast of the United States, in the western Gulf of Mexico, off the northern coasts of Colombia and Panama, and along the Pacific coast of Central America from Panama to Acapulco, Mexico.

From studies of the western North Atlantic, Tucholke, Bryan, and Ewing (1977) identified two high-amplitude reflecting horizons that are conformable with the seafloor and about 500 to 600 m beneath it. These horizons show the following characteristics: they cut across bedding-plane reflectors in the same manner as the reflector horizon observed on the Blake-Bahama Ridge; they appear to be restricted to areas where sedimentary strata dip landward; and their subbottom depth increases with the seafloor depth, a relation consistent with theoretical predictions of the configuration of a hydrate zone (fig. 4). A zone of gas hydrates may overlie the anomalous horizons, and thus the seismic horizons could be reflectors representing an impedance contrast caused by the downward change from gas hydrate to gas in the sediment. Grantz and others (1976) identified a strong seismic reflector that mimics the bathymetry of the seafloor, 100-300 m beneath it, on the continental slope of the Beaufort Sea north of Alaska. The bottom-simulating reflector was identified in about 60 percent of seismic profiles obtained in water deeper than 400-600 m.

Not all bottom-simulating reflectors can be directly related to the presence of gas hydrates. Although gas hydrates provide one reasonable explanation for bottom-simulating reflectors, these acoustic features may also result from temperature controlled diagenetic effects. During DSDP Leg 19, Scholl and Creager (1973) noted seismic reflectors that tend to parallel the seafloor in some Bering Sea sediments draped on the Umnak Plateau, and they coined the acronym BSR for the bottom-simulating reflector. At two sites, 184 and 185, the reflector was penetrated. Although methane was observed in sediment from Site 185, no other evidence for gas hydrates was noted. Scholl and Creager (1973) attribute this reflector to a lithologic transition from hemipelagic diatom ooze to indurated claystone. Because of the time-transgressive nature of this horizon, this BSR appears to represent some sort of migratory diagenetic boundary related to the dissolution of diatoms and the formation of claystone. Hein and others (1978) confirmed that opal-A is transformed to opal-CT in the temperature range corresponding to a subbottom depth of 600 m, the depth of the BSR in Bering Sea sediment. Further, because the subbottom depth of the BSR on the flanks of Umnak Plateau decreases with increasing water depth, this BSR is probably not directly caused by gas hydrates (Shipley and others, 1979). Nevertheless, gas hydrates may still play an important role in the formation of this BSR. Claypool and Kaplan (1974) note that, in all cases of BSR's described from the Bering Sea, the lithologic change is consistent with the inferred depth of the isotherm where gas hydrate would decompose under the prevailing pressure conditions. Claypool and Kaplan (1974) suggest at least an indirect link between lithification and gas hydrate. Free carbon dioxide and methane concentrations determine the pH of interstitial water. The pH conditions determine the solubility of lithologic components such as carbonate and silica. Gas hydrate formation may influence carbon dioxide and methane activities and may therefore influence the dissolution and reprecipitation of carbonate and silica cements.

Thus, some bottom-simulating reflectors are not directly related to the presence of gas hydrates, as illustrated above, but bottom-simulating reflectors may not be observed even though gas hydrates are present. For example, in areas where sedimentary stratification parallels the seafloor, the bottom-simulating reflector may not be detectable. During drilling on DSDP Leg 67 in the Mid-America Trench off Guatemala, gas hydrates apparently were encountered at Sites 497 and 498, but the seismic records for these areas showed no obvious bottom-simulating reflectors (R. von Huene, oral commun., 1979).

Gas hydrate zones in the seafloor may form regionally extensive impermeable seals and may trap economically important accumulations of natural gas, provided sufficient sources for methane are present. If gas were to migrate upward and be impeded by hydrate, it would accumulate at the lower boundary of the hydrate zone as free gas and would cause a significant decrease in seismic velocity at that boundary (Bryan, 1974). Bottom-simulating reflectors are strongest in the vicinity of ridge crests and tend to fade out on the flanks (Markl and others, 1970), a configuration that suggests gas accumulation at the crest as in an anticlinal trap.

OTHER SEISMIC EVIDENCE FOR GAS HYDRATES IN OCEANIC SEDIMENTS

Seismic features other than bottom-simulating reflectors may be produced by gas hydrates. These features include bottom-parallel bright spots, pagoda structures, and deep-water velocity amplitude features (VAMP's). White (1977) suggested that seismic bright spots (amplitude anomalies) in the Gulf of Oman are caused by natural gas accumulations. These subbottom reflectors are curved, mimic the topography of the seafloor, and transgress local bedding (making these bright spots similar to bottom-simulating reflectors, but of lesser lateral extent). White (1979) inferred that the gas is held in place not by a stratigraphic trap but by an impermeable gas hydrate layer that follows the seafloor topography.

Emery (1974) has suggested that pagoda structures may be related to gas hydrates, although these are very shallow subbottom seismic features, and there is little consensus regarding their significance. Geophysical traverses across nearly flat mud bottom at depths between 2,000 and 5,000 m off western Africa provided extensive seismic shallow-penetration recordings at 3.5 kHz. The recordings reveal the presence of common alternating light and dark triangular seismic features, or pagoda structures, whose internal structure and acoustic properties may, according to Emery (1974), be due to local centers of gas hydrate induration.

Velocity-amplitude features (VAMP's) are acoustic anomalies showing narrow (1 to 2 km) subsurface columns of concave reflection horizons called pulldowns, associated with gently arched, high-amplitude horizons higher in the section (Scholl and Cooper, 1978). These kinds of acoustic anomalies, common on seismic profiles collected in the Bering Sea, are typically seen in flat-lying beds at subbottom depths greater than 500 m and in deep water around 4,000 m. VAMP's are essentially deep-seated "bright spots" underlain by reflection horizon pulldowns. Gas hydrates may be responsible for VAMP's by contributing to the restriction of upward-migrating gas and fluids.

It is difficult to detect gas hydrates by purely chemical and seismic means. Support for the identification of gas hydrate in seafloor sediments will result when cores containing hydrates recovered at their subsea temperatures and pressures can be analyzed. A pressure core barrel capable of this task has been designed by DSDP but has never been successfully deployed in a gas hydrate horizon. From the geologic, geophysical, and geochemical evidence obtained thus far, there is little doubt that gas hydrates are an important part of the marine sedimentary record.

SELECTED BIBLIOGRAPHY

The following is a selected bibliography containing the references cited in this paper along with other papers dealing with the physical chemistry, geology, and geophysics of gas hydrates. This bibliography does not represent an exhaustive search of the literature, but rather includes those pertinent papers readily available to us.

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