22. ANALYSES OF OIL AND CAP ROCK FROM CHALLENGER (SIGSBEE) KNOLL

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CONTENTS

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[1] Numbers in parentheses after each heading refer to the relevant part of Section 1 of this chapter.

ABSTRACT

Analyses of Deep Sea Drilling Project Cores 5 and 6, Leg 1, Site 2 indicate that a bona fide crude oil exists in the Challenger Knoll in a normal cap rock environment. These conclusions are based upon oil composition, rock characteristics and isotopic data.

The lithology of Core 5 is calcite at the top with calcite and sulfur at the base. Material recovered in Core 6 is gypsum. The calcite portion of Core 5 contains a low gravity, high sulfur oil which is highly aromatic and highly asphaltic—consistent with other low gravity petroleums. The known Gulf Coast Tertiary crude oils with high sulfur appear to be associated with salt dome cap rock. The Challenger Knoll oil has some unusual characteristics which, however, are shared by some known cap rock oils produced from the Gulf Coast Tertiary. Some unusual deficiencies in *n*-paraffins occur in the liquid petroleum gas and the virgin naphthas. The C_4, C_5, C_6 and C_7 hydrocarbons are deficient in *n*-paraffins relative to the corresponding isomers. The profile of the C_7 hydrocarbons as a percentage of C_7 saturates in the Challenger Knoll oil is similar to that in known Tertiary cap rock oils from the Spindletop and Stratton Ridge fields produced from Gulf Coast Tertiary sediments.

The molecular size distribution of *n*-paraffins throughout the Challenger Knoll oil is low in both the very heavy and very light molecular sizes leaving most of the *n*-paraffins in the intermediate C_{13} through C_{24} range. The heavy *n*-paraffins, including C_{24} and larger, have a smooth distribution indicating no odd carbon preference which is consistent with most oils; also, the intermediate size *n*-paraffins have no odd or even predominance. In this molecular size range (C_{13}-C_{24}), however, a predominance of odd-carbon numbered normal paraffins has been noted in some petroleums. Other compound type distributions are within the range observed for natural petroleums.

The Challenger Knoll oil is believed to be a young oil of marine origin. Carbon isotope data and molecular size distributions of the porphyrins are consistent with an origin of marine derived organic material. A high cyclohexanes to cyclopentanes ratio and a close similarity of C^{13} abundance between the saturated hydrocarbons (-26.5 o/oo), aromatic hydrocarbons (-26.8 o/oo), polar NSO compounds (-26.5 o/oo), and asphaltenes (-26.8 o/oo) provide some of the evidence for a young, immature oil.

The calcite-sulfur zone at the bottom of Core 5 contains 19 per cent elemental sulfur. Sulfur in cap rock is known to have a biogenic origin which requires the presence of organic matter (petroleum) and sulfates for the bacterial reduction of sulfates to hydrogen sulfide, which is then oxidized to free sulfur. Another product of the process is calcite, containing carbon, which was originally in the petroleum. In this process, the sulfate reducing bacteria are known to fractionate or change the relative abundance of the sulfur isotope S^{34}. The sulfur isotope data on the gypsum, on the hydrogen sulfide collected with the core, and on the free sulfur is consistent with the biogenic reduction of the sulfate and subsequent oxidation of hydrogen sulfide to free sulfur. Also, the C^{13} abundance in the calcite identifies the calcite carbon as having its origin in the cap rock oil. Sulfate reducing bacteria were identified in the gypsum; however, contamination could be the source of these bacteria. The source of the oxidizing agent for oxidizing hydrogen sulfide to sulfur in a cap rock environment is an unanswered question.

Cap rock is thought to form from the relatively insoluble residues which collect on top of a salt dome as it protrudes into water, which dissolves and removes the salt. A number of these resistant mineral assemblages typical of salt dome cap rock were found in the Challenger Knoll. These include detrital quartz, doubly terminated quartz crystals, quartz rosettes and tourmalne. Quartz crystals, nearly identical to these, are common in the Louann salt.

The crystal habit, structure, paragenesis, replacement relationships and mineral associations of calcite, gypsum and sulfur are similar to those in Gulf Coast cap rock.

Abundant pollen grains and spores were recovered which apparently had concentrated with residues in the cap rock as the salt was dissolved and carried away. The assemblage consists mainly of *Classapollis* spp. and *Exesipollenites tumulus* Balme. The age of the assemblage is identified as probably Middle or late Jurassic, but could be early Cretaceous.

SECTION 1: RESULTS AND GENERAL DISCUSSION

INTRODUCTION

After recovery of the oil saturated core from Site 2 of Leg 1 of the Deep Sea Drilling Project, the Chief Scientists, Drs. Maurice Ewing and J. Lamar Worzel, recommended that analyses be made by laboratories competent to examine petroleum saturated samples. Accepting this recommendation, the Project sought the advice of the JOIDES Planning Committee and it was agreed that the most effective approach to this matter would be to request the advice of the American Petroleum Institute. Mr. Roy F. Carlson, Director of the Institute, recommended that the A.P.I. appoint a small committee to plan the analysis program and nominate a lead laboratory. The JOIDES Planning Committee requested that the JOIDES Advisory Panel on Pore Water and Organic Geochemistry meet with representatives of the A.P.I. to discuss the details of the analyses. The Planning Committee determined that the results of such analyses were to be a part of the core description report.

On October 1, 1968, Dr. John M. Hunt of Woods Hole Oceanographic Institution, Chairman of the JOIDES Advisory Panel on Pore Water and Organic Geochemistry met with Mr. Carlson of the A.P.I. and administrative representatives of Shell Development Company, Esso Production Research Company, Mobil Research and Development Corporation and Chevron Oil Field Research Company in Houston, Texas. At this meeting it was recommended that the laboratories of Mobil, Shell and Esso should comprise a committee for analyses of the oil saturated core with Mobil as the lead laboratory. Chevron and Phillips Petroleum Company Research Center offered their help. Three days later, Dr. Hunt met with the laboratory representatives of Shell Development Company, Esso Production Research Company and Mobil at the Mobil Research Laboratory in Dallas, Texas. A plan was outlined and agreed upon for sharing the work on analyses of the cores.

The following report is a compilation of data from rock and fluid analyses of Cores 5 and 6 from Challenger Knoll (Deep Sea Drilling Project Leg 1, Site 2) carried out by the petroleum company laboratories. The primary purposes were to determine if the oil and the apparent cap rock were similar to other oils and cap rocks and, if possible, to find evidence for the age of the cap rock. It was believed that these purposes could be accomplished most effectively by using the experience and analytical methods available in petroleum company laboratories for identifying and classifying the gas, oil and rock components associated in the core samples. The laboratories which participated in these analyses included those of Mobil, Esso, Shell, Phillips, Chevron and Mellon Institute, in coordination with Mr. Carlson and Dr. Hunt.

This compilation consists of two sections. The first section: outlines the analyses; presents the salient features; places them in perspective with the various contributions; and, guides the reader to appended discussions, which appear in the second section–data and methods–and which apply specifically to particular analyses. Reports in the second section were prepared by the participating laboratories and are cross-referenced with the first section.

1.1 ANALYTICAL METHODS AND RESULTS

1.1.1 Core Samples Analyzed

1.1.1.1 Core 5

Two core samples designated 1-02-05-1 (Core 5-1) and 1-02-05-2 (Core 5-2) were received for analysis. Core 5-1, 34 inches (86.5 cm) long, was largely unconsolidated calcite crystals coated with oil. Core 5-2, 18 inches (45.8 cm) long, consisting of calcite and sulfur crystals was somewhat mixed due to handling and shipment.

Core 5-1 and Core 5-2 were each sectioned in half longitudinally. However, prior to longitudinal sectioning of Core 5-1, the entire interval between 15½ inches to 17 inches (39.4 cm - 43.3 cm)–from bottom–was removed for an archive plastic mount. Longitudinal half-sections of Core 5-1 and Core 5-2 were maintained as archive specimens (Plate 1).

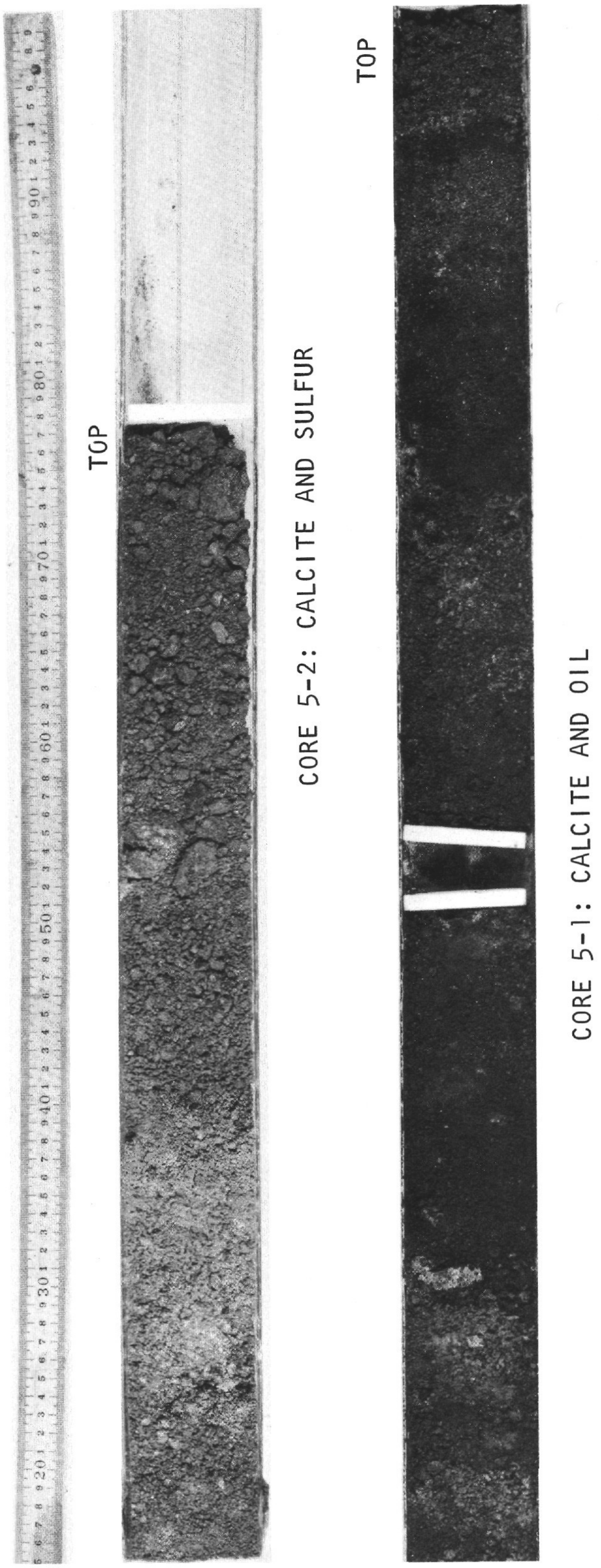


Plate 1. *Archive halves of Cores 5-1 and 5-2, Core 5-2 immediately underlies Core 5-1. A short coherent interval of Core 5-1 has been removed for an archive plastic mount.*

The Core 5-2 half-section was longer than the original 18 inch (45.8 cm) core sample because only the bottom 13 (33.1 cm) inches could be longitudinally sectioned; the loose, mixed upper portion of Core 5-2 was allowed to form the upper portion of the archive specimen accounting for a length of 24 (61.2 cm) inches.

For analytical purposes, samples of a longitudinal half-section of Core 5-1 were removed sequentially in approximately 3 inch (7.6 cm) half-sections from the top of the 34 inch (86.5 cm) core to the bottom. Each of these samples was extracted for oil leaving the rock matrices intact (see Section 2.1). Total oil recovery was 46.0 grams. The bottom 13 inch (33.1 cm) half-section of Core 5-2 (see description above), which was removed for analytical purposes, was considered by the participating laboratories as a composite sample because of its somewhat mixed condition. This 13 inch (33.1 cm) half-section was divided into thirds longitudinally, and the center portion was homogenized for native sulfur analysis. Sulfur recovery was 19 per cent. The other two-thirds of the 13 inch (33.1 cm) half-section was maintained for petrographic, mineralogic and other analyses.

Below are brief descriptions of Core 5-1 and Core 5-2:

Core 5-1:
Core 5-1 (1-2-5-1) 0 inches (Bottom) to 34 inches (Top) (0 cm - 86.5 cm), consists predominantly of calcite crystals (euhedral, 1 mm±) coated with oil. No sulfate is apparent. Residue after oil extraction and carbonate dissolution is 2.8 per cent and is composed primarily of amorphous organic material, containing traces of quartz and pyrite.

34 inches - 31 inches (86.5 - 79 cm) - yellowish brown, calcite, no sulfur observed.
31½ inches - 32 inches (80.2 - 81.5 cm) - brownish black streaks ½ inch thick.
31 inches - 28 inches (79 - 71.3 cm) - yellowish brown, calcite, no sulfur observed.
28 inches - 25 inches (71.3 - 63.7 cm) - brownish black.
25 inches - 23 inches (63.7 - 58.6 cm) - brownish black.
23 inches - 20 inches (58.6 - 50.9 cm) - yellowish brown, slightly lithified particles.
20 inches - 17 inches (50.9 - 43.3 cm) - brownish black.
17 inches - 15½ inches (43.3 - 39.5 cm) - entire section removed for archive plastic mount.
15½ inches - 12 inches (39.5 - 30.6 cm) - brownish black.
12 inches - 9 inches (30.6 - 22.9 cm) - brownish black.
9 inches - 6½ inches (22.9 - 16.6 cm) - brownsih black grades to yellowish brown, contains lithified ½ inch thick portion.
6½ inches - 5 inches (16.6 - 12.7 cm) - yellowish medium brown.
5 inches - 3 inches (12.7 - 7.6 cm) - brownish black grades to yellowish brown.
3 inches - 0 inches (7.6 - 0 cm) - yellowish brown grades to dark brown, no sulfur observed.

Core 5-2:
Core 5-2 (1-2-5-1) 0 inches (Bottom) to 24 inches (Top) (0 cm - 61.2 cm), consists of calcite and sulfur crystals. No sulfate is apparent. Residue after sulfur extraction and carbonate dissolution is 0.5 per cent and is composed primarily of amorphous organic material, containing traces of quartz and pyrite.

24 inches - 13 inches (61.2 - 33.1 cm) - unconsolidated, *mixed*; lithified portions up to 1 inch diameter; brown; sulfur and calcite crystals.
13 inches - 0 inches (33.1 - 0 cm) - essentially unconsolidated; sulfur and calcite crystals; sulfur crystals particularly evident between 9 inches to 4 inches (22.9 - 10.2 cm).

A core-catcher sample (approximately 300 grams) was also received which is part of the bottom of Core 5-2. It is unconsolidated and contains a few hard lumps of calcite and small sulfur crystals.

1.1.1.2 Core 6

Core 6 (1-2-6) consisted of about 10 lumps in the order of one square inch (2.5 cm x 2.5 cm) of oil-stained gypsum. This was the entire sample received. The Core 6 sample was taken somewhere in a 15 foot (4.57 m) interval below Core 5-2.

1.1.2 Analytical Flow Chart

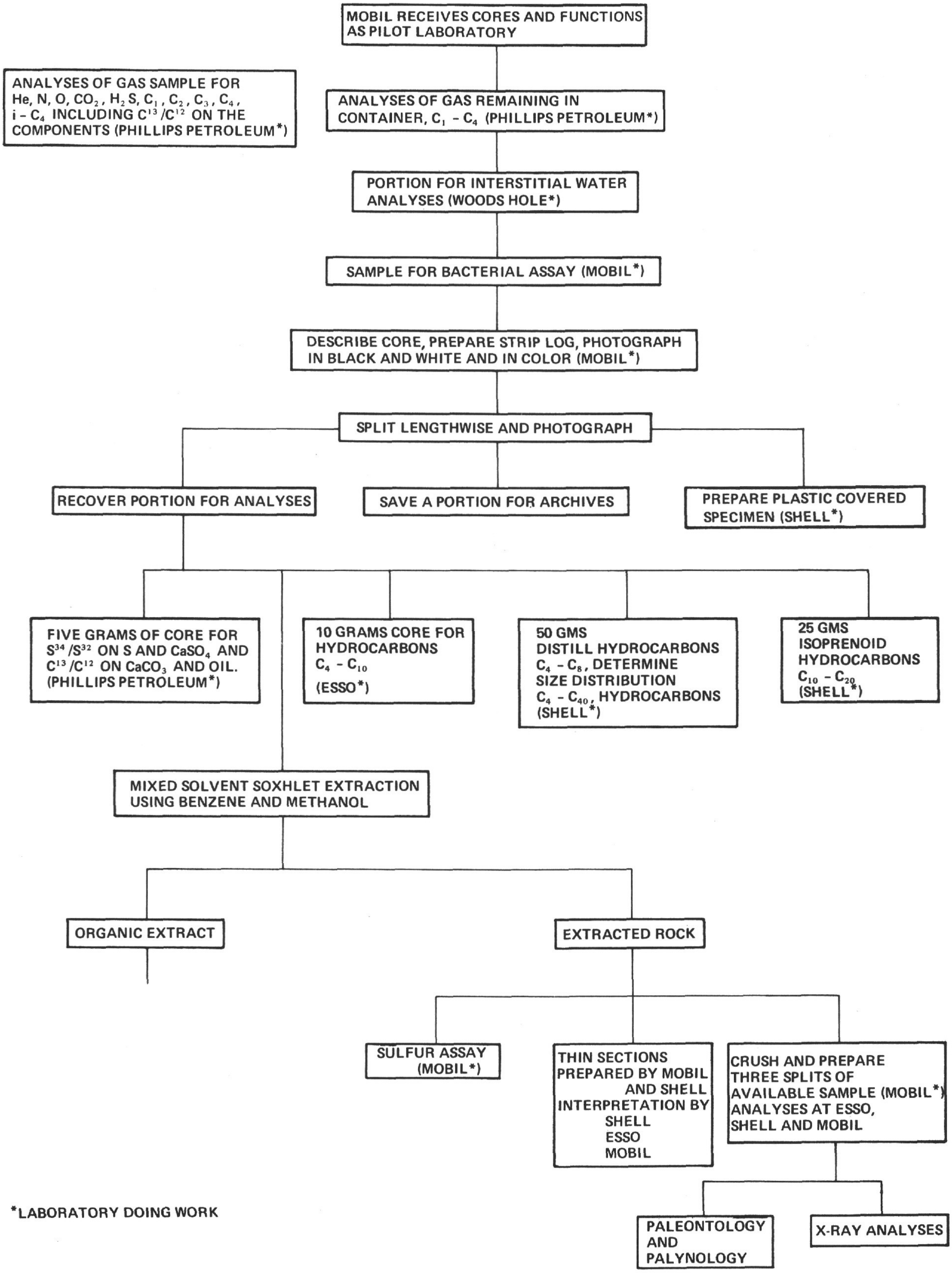
An outline of the analytical work on Deep Sea Drilling Project Cores 5 and 6, Leg 1, Site 2 is given in the form of a flow chart (Figure 1).

1.1.3 Rock Characteristics

1.1.3.1 Petrologic and Micropaleontologic Examination of Cores 5 and 6

See Section 2.2 and Section 2.3. The mineralogy of the two cores investigated is typical of the transition zone of a cap rock and indirectly supports the presence of halite beneath the predominantly detrital sediments which mantle the Sigsbee Abyssal Plain. The transition zone of Gulf coast cap rock is characterized by sulfur, gypsum, calcite, petroleum and hydrogen sulfide, all of which were found in Cores 5 and 6, and is that part of the cap rock in which active alteration of anhydrite to gypsum, calcite and sulfur occurs. Minerals identified in Core 5 included calcite, sulfur, pyrite, dolomite, quartz and tourmaline. Core 6 consisted primarily of gypsum. A summary of characteristics and mode of occurrence of these minerals and numerous photomicrographs of specimens of the cores are included in Section 2.3.

Palynomorphs of Jurassic or early Cretaceous time were identified and photomicrographs of these specimens



*LABORATORY DOING WORK

Figure 1. *Flow diagram for analyses of core samples from the Challenger Knoll, Gulf of Mexico.*

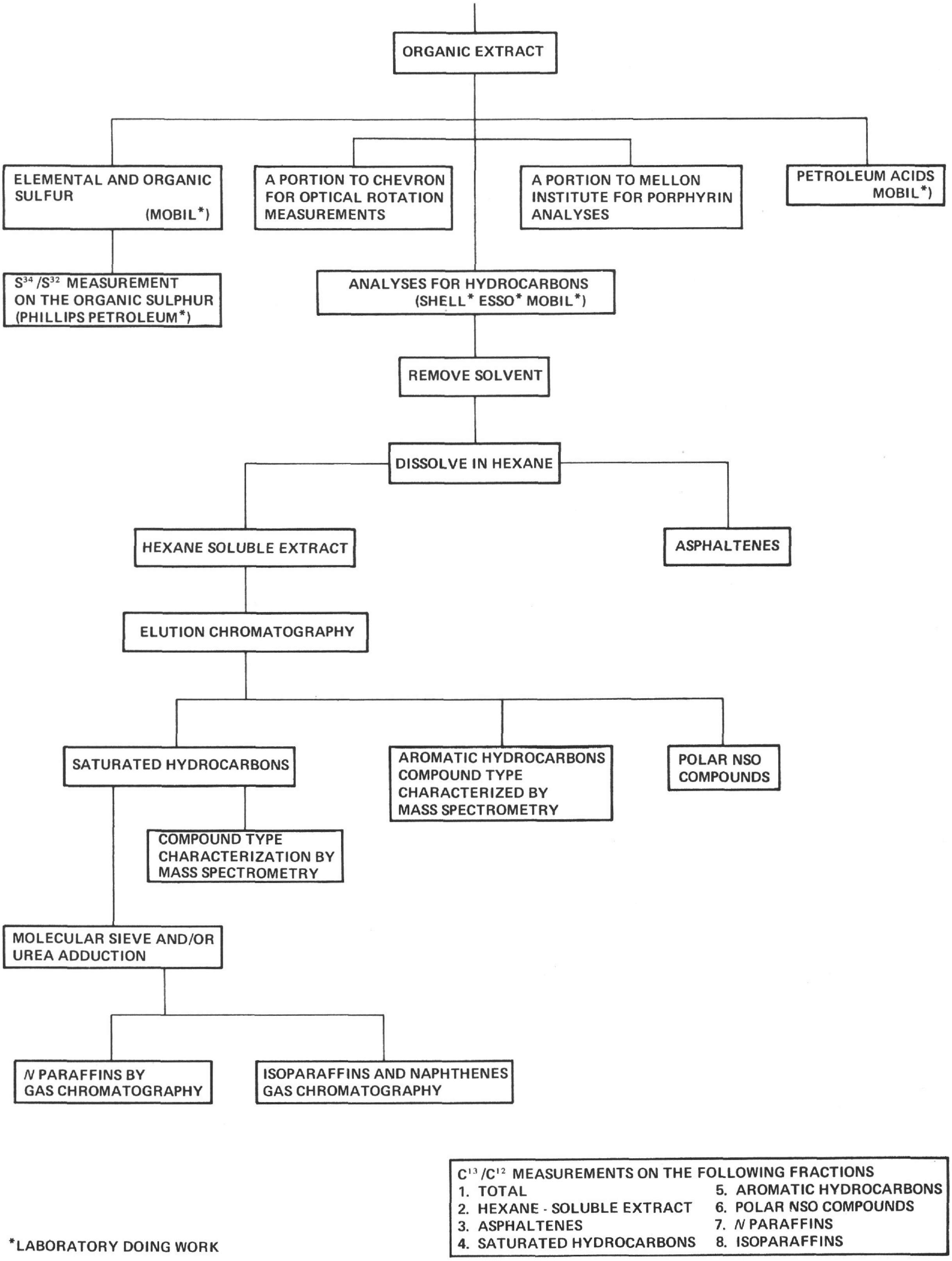


Figure 1 - *continued.*

and discussion concerning them are included also in Section 2.3.

1.1.3.2 Sulfur Isotope Analyses

Sulfur isotope analyses of gypsum from Core 6, hydrogen sulfide in gas from Core 5-1, elemental sulfur from Core 5-2, and organic sulfur in the oil from Core 5, were made at the Phillips Research Laboratory, Bartlesville, Oklahoma. Data for two pyrite samples from Core 4 have been included for comparison. These and mineralogical data are discussed in Section 2.4. The sulfur isotope data are similar to data reported for Gulf Coast salt dome sulfur deposits by Thode *et al.* (1954) and by Feely and Kulp (1957). Such data are believed to indicate the biogenetic reduction of gypsum to hydrogen sulfide with the subsequent partial oxidation of the hydrogen sulfide to elemental sulfur. Part of the sulfur is deposited in the cap rock, and the remainder dissolves in and partially reacts with the oil thereby increasing its aromaticity and decreasing the API gravity.

1.1.4 Bacterial Assay

1.1.4.1 Core 5

Bacterial analyses were made of both the oil-bearing portion of Core 5 (designated 5-1) and the sulfur-bearing portion (designated 5-2). An approximate 1-gram sample was removed aseptically from the bottom of each section. These two samples were analyzed for sulfur-oxidizing bacteria, sulfate-reducing bacteria and general aerobic and anaerobic microflora. The various culture media and the means of taking the bacteriological samples are described in Section 2.5.

No sulfur-oxidizing bacteria, sulfate-reducing bacteria, or any bacteria capable of growing under anaerobic conditions were definitely detected in Core 5-1 or Core 5-2. However, large numbers of gram-negative, motile, non-sporeforming aerobic bacteria (0.5 microns by 1.5 microns) were found in the sample from the bottom of Core 5-1. The sample from the bottom of Core 5-2 was negative.

Sample, at Bottom of Core	Aerobic Bacteria Per Gram of Core
Core 5, Section 1	4×10^6
Core 5, Section 2	0

Further bacteriological tests of Core 5 (Sections 1 and 2) were made by analyzing small samples taken at intervals along the core sections.

Sample	Aerobic Bacteria Per Gram of Core[1]
Core 5-1, 2 inches (5.1 cm) from bottom	3×10^6
Core 5-1, 7 inches (17.8 cm) from bottom	5.6×10^6
Core 5-1, 15 inches (38.2 cm) from bottom	18×10^3
Core 5-1, 20 inches (51 cm) from bottom	2.6×10^6
Core 5-1, 22 inches (56 cm) from bottom	0
Core 5-1, 33 inches (84.1 cm) from bottom	8.6×10^5
Core 5-2, 1 inch (2.54 cm) from bottom	1.5×10^6
Core 5-2, 2 inches (5.1 cm) from bottom	6×10^4
Core 5-2, 8 inches (20.3 cm) from bottom	2×10^3
Core 5-2, 15 inches (38.2 cm) from bottom	1.2×10^4

[1] RI agar medium employed (see Section 2.5).

The bacterial numbers observed are much higher than anticipated if they were due directly to contamination from seawater or handling. These numbers indicated growth of the bacteria within the core sample, although it is quite likely that such growth occurred after the sample was taken.

1.1.4.2 Core 6

Core 6, which consisted of lumps of oil-stained gypsum or anhydrite, was found to contain sulfate-reducing bacteria (100/gram). A lump of the gypsum was broken open and the bacteriological sample was removed from the interior as aseptically as possible. No precautions had been taken previously to prevent bacterial growth in the sample or to prevent contamination. For these reasons, no tests were made of the general microflora. The presence of sulfate-reducing bacteria in Core 6 may be significant, but their presence in the core material due to contamination is definitely a possibility.

1.1.5 Fluid Characteristics

1.1.5.1 Associate Gases

Two gas samples were collected from Core 5. The first sample (Gas Sample 1) was procured shortly after the core was brought on board the *Glomar Challenger.* The second (Gas Sample 2) was obtained from the plastic core liner several weeks later and immediately prior to partition of the core at the Mobil Laboratory. Both samples were submitted to Phillips Petroleum Research Center for analysis (see Section 2.6). The carbon isotopic compositions of the first five members of the hydrocarbon series in Gas Sample 1 and the first three in Gas Sample 2 are plotted versus carbon number, and compared to values for the topped oil and calcite from Core 5, Section 1. Data for the light hydrocarbons in two petroleums, both underlain by salt, are provided by comparison. Values are relative to the Peedee belemnite reference. Comment from the Phillips laboratory is that: "The component composition is typical of a gas associated with a crude oil of intermediate API gravity. The shape of the curve representing carbon isotopic composition versus carbon number is normal for young but well-developed crude oils. The isotopic composition of the 'topped' extracted oil is intermediate in the range attributed to a marine environment of deposition."

1.1.5.2 Oil Composition

One-half (longitudinal section) of Core 5, Section 1 weighing a total of 1581 grams was extracted with benzene-methanol in soxhlet extractors. The methanol was subsequently removed from the benzene extract by washing with water. The total amount of oil in the benzene extract was 46.0 grams (2.9 per cent by weight of the core material extracted). These extraction methods are outlined in Section 2.1, previously referred to.

Analysis of the oil by the various petroleum laboratories was approached by different methods. There was agreement, however, as to the gross composition of the oil. The oil is similar to some oils previously characterized. The heavy hydrocarbon fraction is low in normal paraffins and the oil can be classified generally as aromatic.

1.1.5.2.1 Volatility and Hydrocarbon Type Distribution

Volatility distribution of hydrocarbons C_5 through C_{34} was determined by the Shell laboratory for oil (designated Sample GM-S-101) extracted from a part of Core 5-1. This volatility distribution is shown in table and graph form in Section 2.7. The volatility distribution was calculated from the results of two determinations: one was done on the rock fluid, the other on the extract. The data shown are for the combined results for GM-S-101 and GM-O-101. Hydrocarbon type distribution for Sample GM-O-101 (extract composite) is indicated also in Section 2.7. Section 2.7 is a general discussion of the analyses performed by the Shell laboratory and includes data for sulfur analysis, asphaltene determination, C_{10} through C_{20} normal paraffins and isoprenoid-isoparaffins, and a comparison between the Challenger Knoll oil and two low-gravity Gulf Coast Tertiary oils.

Section 2.8 includes data and discussion of the composition of Challenger Knoll oil, prepared by Esso Production Research Company. These data include C^{13} to C^{12} ratios.

1.1.5.2.2 Petroleum Acids

The acidic fraction of the oil from Challenger Knoll was extracted according to the method described in Section 2.9. The petroleum acids total about 0.29 per cent by weight of the oil. For comparison, eight Tertiary petroleums from the Texas Gulf Coast area contain 0.0015 to 0.0396 per cent petroleum acids with an average of 0.018 per cent.

1.1.5.2.3 API Gravity

Gravity of oil from Core 5-1 was determined using a 2 milliliter pycnometer.

Specific gravity at 78° F (25.6° C) = 0.9604 g/cc
at 60° F (15.6° C) = 0.9667
API gravity = 14.8

1.1.5.2.4 Organic Sulfur

The organic sulfur in oil from Core 5-1 was determined after free sulfur was removed with sodium cyanide in a methanolic solvent system. This organic sulfur content of the solvent-free oil, determined by the oxygen-bomb combustion method (ASTM Method D-129-60) at Mobil's Field Research Laboratory, was 3.74 per cent. The amount of free sulfur in the extract was 1.24 wt % of the oil, giving a total sulfur content of 4.98 per cent for the solvent-free extraction residue (organic sulfur plus free sulfur). Discussion of this analysis is in Section 2.10.

1.1.5.2.5 Low Boiling Hydrocarbons

Data concerning hydrocarbons in the C_4 through C_{10} range are presented in Section 2.7 and Section 2.8. Variations in these data can be accounted for on the basis that samples from different parts of Core 5 were analyzed and the method of analysis likewise differed. The Esso sample was heavily saturated with oil, while the Shell sample was low in oil content. This may explain why the value in amount of material lower than C_{10} reported in the Shell data is so much less than is reported in the Esso data.

1.1.5.2.6 Hydrocarbon Type Analyses of Heavier Oil Fraction

Hydrocarbon group-type analyses are discussed in Section 2.7, Section 2.8 and Section 2.11, which include contributions of four laboratories. Although there were four different approaches to the chromatographic separations of the heavier oil components, the reported amounts of saturated hydrocarbons, aromatic hydrocarbons, NSO asphaltic compounds and asphaltenes can be reconciled and are in reasonable agreement. This is demonstrated by the data in Table 1, excerpted from the appended results.

By the use of high resolution mass spectrometry, Esso found the aromatic fraction determined by the second method (Table 1) to contain 23.4 per cent hetero compounds. If this correction is made, the aromatic hydrocarbon fraction is reduced from 41 per cent to 31.2

TABLE 1
Chromatographic Separations of the Heavier Oil Components

Contributor	Saturated hydrocarbons	Aromatic hydrocarbons	Hetero compounds	Asphaltenes
Shell Development Company (Section 2.7)	30%	37%	19%	14%
Esso Production Research (Section 2.8)	33%	41%	12%	14%
Mobil Research (by method of Middleton, Table 18, Section 2.11)[a]	26%	41%	18%[b]	15%[c]
Mobil Research (by silica gel chromatography, Section 2.11)	27%	37%	21%	14%[c]

[a] based on total extract
[b] hard resin and asphalt
[c] determined by difference (includes material remaining on column)

per cent and the hetero compound fraction is increased to 21.8 per cent.

It is interesting to note the proportions of aromatic hydrocarbons in the total hydrocarbons (aromatic plus saturates) for the different methods in the table above. These proportions are 55 per cent, 55 per cent, 61 per cent and 58 per cent for the methods, respectively. In Figure 2 the per cent distributions of aromatic hydrocarbons in total hydrocarbons for the C_{18}+ portions of a large number of crude oils are shown as determined by silica gel chromatography (method of Section 2.11).

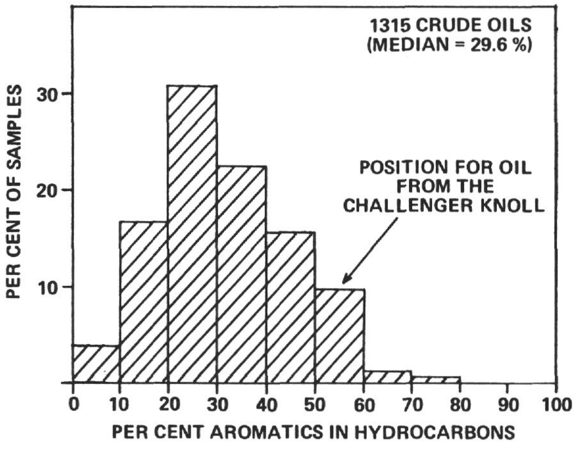


Figure 2. *Distribution of per cent aromatic hydrocarbons in total hydrocarbons for the* C_{18}+ *fractions of crude oils.*

The oil from the Challenger Knoll is within the distribution for crude oils although it is on the high aromatic side, indicating it to be a highly aromatic crude oil.

Compound-type characterization of the heavier saturated hydrocarbons by mass spectroscopy was done by each of three contributing laboratories (Shell, Esso, Mobil). Methods for separating the heavy saturated hydrocarbons were different for the three laboratories and yielded fractions with different average volatility cut-off points (see Sections 2.7, 2.8 & 2.11). In spite of these differences and slightly different mass spectrometer methods, the composition profiles for the noncondensed naphthenes, 2-ring naphthenes, 3-ring naphthenes, 4-ring naphthenes, 5-ring naphthenes and 6-ring naphthenes are generally similar for the three sets of analyses. This is illustrated in Table 2 in which data from the three laboratories have been normalized to 100 per cent for the heavier saturated fractions.

TABLE 2
Compound-Type Analysis of Heavier Saturated Hydrocarbons

Compound Type	Composition (Per Cent Saturated Hydrocarbon Fraction)		
	Esso	Shell	Mobil
Paraffin	32	28	37
Noncondensed naphthene	35	22	27
2-Ring naphthene	18	19	17

TABLE 2 - *Continued*

Compound Type	Composition (Per Cent Saturated Hydrocarbon Fraction)		
	Esso	Shell	Mobil
3-Ring naphthene	9	13	10
4-Ring naphthene	4	12	6
5-Ring naphthene	2	4	2
6-Ring naphthene	<1	1	-
Mono-aromatic	-	1	2
Estimated average stabilization cut-off-point	$C_{13}+$	$C_{18}+$	$C_{10}+$

1.1.5.2.7 Porphyrins

Porphyrin analysis was carried out by E. W. Baker of Mellon Institute of Carnegie - Mellon University. A spectrum of the vanadyl petroporphyrin fraction from Challenger Knoll crude oil is included in Section 2.12. The UV-visible and mass spectra (see Section 2.12) of the vanadyl petroporphyrin fraction is typical of that of a petroleum of Tertiary marine origin.

1.2 IMPLICATIONS AND COMPARISONS

1.2.1 Comparison with U. S. Gulf Coast Cap Rock

Gypsum, calcite and sulfur are the major minerals in Cores 5 and 6, and they are also the major minerals in the upper part of U. S. Gulf Coast cap rocks. In Cores 5 and 6 the crystal habit, structure, paragenesis, replacement relationships and mineral associations of these minerals are similar to those described for Gulf Coast cap rock. Furthermore, the quantity and mode of occurrence of the minor minerals, pyrite, dolomite and quartz, are nearly identical with Gulf Coast cap rock. Petroleum and hydrogen sulfide, which are commonly found in cap rock, are also present filling pores in Core 5. A more detailed comparison of Cores 5 and 6 and Gulf Coast cap rock is included in Section 2.3.

1.2.2 Comparison with Known Oils

The oil from Challenger Knoll is similar in composition to some known oils. Although there are similarities between Challenger Knoll oil and two Gulf Coast Tertiary oils, particularly a cap rock oil (see Section 2.7), it does not necessarily follow that Challenger Knoll oil is Tertiary; it could be older. These comparisons and other data are significant, however, in demonstrating that the oil from Challenger Knoll is, in fact, a bona fide oil. For example, as pointed out in Section 2.7, there is no odd carbon preference in the *n*-paraffins of Challenger Knoll oil which is consistent with most oils.

In paraffin crude oil components boiling through 111° C, the normal isomers are usually present in the highest proportions (Martin *et al.,* 1963); however, in the case of the Challenger Knoll oil and the two Tertiary oils from the Spindletop and Stratton Ridge fields, this is definitely not the case. The normal C_6 and C_7 isomers are decidedly in the minority (Sections 2.7 and 2.8). In many cases for crude oils the C_7 paraffin components decrease as branching increases (Martin *et al.,* 1963).

As illustrated in Figures 3 and 4, the order of C_7 isomers in the Challenger Knoll oil is quite unlike the

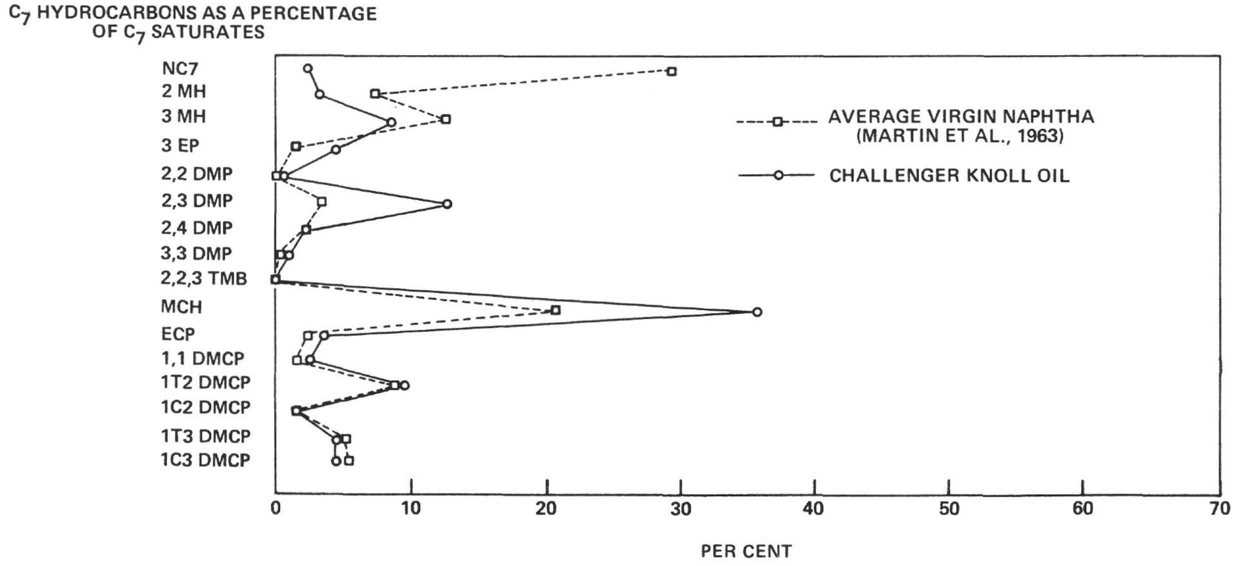


Figure 3. *Comparison of Oil Compositions.*

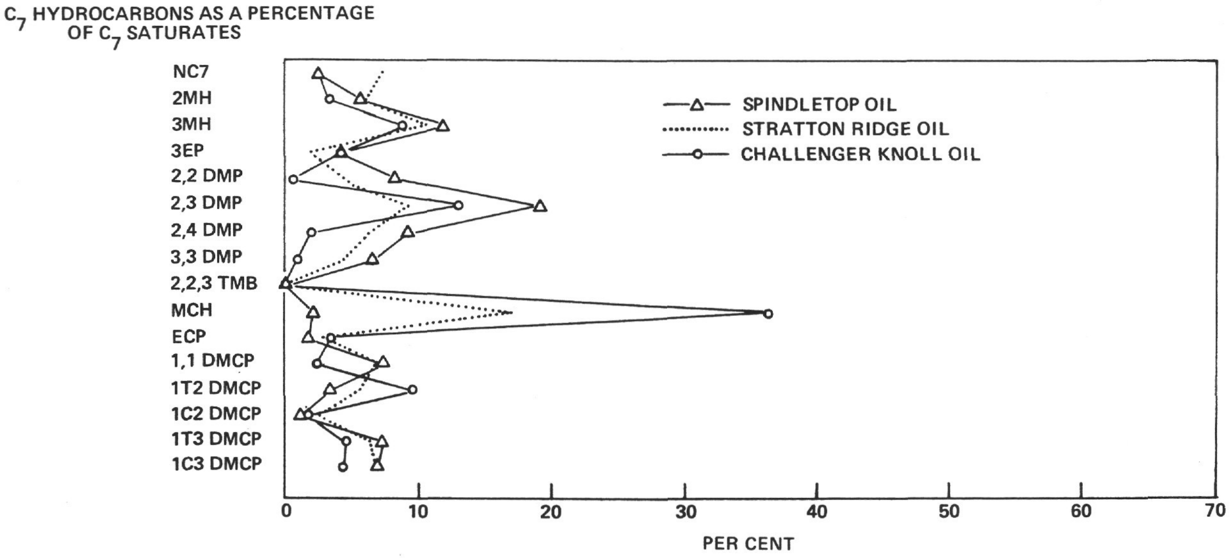


Figure 4. *Comparison of Oil Compositions.*

order in the average virgin naphtha as defined by Martin, but it is more similar to the order in the two Tertiary oils (Spindletop and Stratton Ridge). The Challenger Knoll oil is more like the average virgin naphtha, when one considers the preferred order for dimethylcyclopentanes, than it is like the two Tertiary oils shown.

In comparing further the C_5 through C_7 hydrocarbon composition of the Challenger Knoll oil with the compositions of the eighteen oils studied by Martin *et al.* (1963), the two following observations are made: a) The Challenger Knoll oil most resembles the Middle East Wafra oil, reservoired in a Tertiary carbonate formation. Both oils are high in cyclohexanes and branched paraffins and are low in *n*-paraffins and aromatics. b) The Challenger Knoll oil shows a predominance of cyclohexane types over cyclopentane types. Martin *et al.* have suggested that a high cyclohexanes to cyclopentanes ratio may indicate either a non-marine source or a relatively young crude oil. The latter explanation seems to best fit the Challenger Knoll oil.

The estimated total quantity of C_4 through C_{10} hydrocarbons in the Challenger Knoll oil is about 14 per cent, based on Esso data. Smith *et al.* (1959), have reported ranges of naphtha contents (approximately equivalent to the C_4 through C_{10} fraction) for several oil-producing areas in the U. S., including: Gulf Coast Tertiary, California Tertiary, West Texas Permian, Mid-continent Cretaceous and Paleozoic, Michigan Devonian, and Pennsylvania Devonian. The Challenger Knoll oil is definitely on the lean side for naphtha content, most resembling some of the Gulf Coast and California Tertiary oils. It is possible that the Challenger Knoll oil may have originally contained a greater quantity of these C_4 through C_{10} hydrocarbons, but that some were lost when the core was brought to the surface and during handling between the time it was taken aboard ship and the time it was analyzed in the laboratory. If the naphtha content of the Challenger Knoll oil is truly quite low, this would suggest a rather immature petroleum, one that has not undergone appreciable chemical transformation.

The asphaltene content for the Challenger Knoll oil is rather high at 14 per cent. Erdman (1964) has reported asphaltene contents for thirteen crude oils of widely different geologic histories. Only two of the oils have comparable asphaltene contents: Boscan (Venezuela) Cretaceous (18 per cent) and the Athabasca (Canada) Cretaceous (19 per cent).

The isoprenoid isoparaffins, farnesane, C_{16}, C_{18}, pristane, and phytane appear to be present in the Challenger Knoll oil. From the chromatograms a very rough estimate was made of the pristane/phytane ratio, which is 0.7. Martin *et al.* (1963) have published pristane and phytane contents for seventeen different petroleums of quite varying geological histories. The average pristane/phytane ratio for these oils is 1.3, with a range from 0.6 to 2.2. It is quite interesting to note that among these oils, the three oils with the lowest pristane/phytane ratios (Darius, 0.7; Lee Harrison, 0.6; and Wafra, 0.7) also have the highest sulfur contents (2.7, 3.2, and 4.8, respectively). The Challenger Knoll oil certainly fits in with these three oils. Age, in this case, may not be a factor since the three oils were produced from Cretaceous, Permian, and Tertiary age reservoirs, respectively.

The C^{13}/C^{12} ratio on the total oil is -26.6 o/oo (Section 2.8), relative to the Peedee belemnite standard. Silverman (1964) has published C^{13}/C^{12} ratio ranges of natural carbonaceous materials. He lists the range for petroleum believed to be derived from organic matter deposited in marine environments as -20 to -29 o/oo. The Challenger Knoll oil falls in this range. Feely and Kulp (1957) have published C^{13}/C^{12} data on two Gulf Coast cap rock crude oils from Boling Dome and Lake Washington, which average out -26.3 o/oo and -25.6 o/oo. These values are similar to those obtained on the Challenger Knoll oil.

S. R. Silverman also analyzed the C^{13}/C^{12} ratio in Challenger Knoll oil and got a value of -26.8 o/oo relative to the PBD-1 standard (see Section 2.13).

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SECTION 2: DETAILED DATA AND DISCUSSION[1]

2.1 EXTRACTION OF CORE 5-1 (1.1.1.)

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Apparatus

The apparatus consisted of a soxhlet extraction assembly equipped with glass extraction thimbles containing extra coarse porosity discs.

Solvent

Each soxhlet was charged with 200 milliliters of mixed solvent consisting of 80 per cent benzene and 20 per cent methanol. The initial solvent boiling from the flask formed an azeotrope of approximately 60 per cent benzene and 40 per cent methanol. This mixture was effective in extracting the oil in the presence of water. The amount of solvent was chosen so that the alcohol would be depleted by hold-up in the extraction chamber and pure benzene would enter the extraction thimble toward the end of each extraction cycle. This alteration of solvent composition during the extraction cycle is believed to provide optimum conditions for complete extraction of oil from samples containing variable water contents.

Samples

The longitudial half-section of Core 5-1 was cut into two to three inch (5.1-7.6 cm) sections for extraction of the oil in order to leave the rock matrices intact and sequentially identified for subsequent petrographic examination. The core material was sufficiently porous and unconsolidated that crushing prior to extraction was not necessary.

Extraction

Core sections weighing from 31 to 150 grams were individually extracted for complete recovery as indicated by clear solvent returning from the extraction chamber. This was accomplished in about six hours.

Extracts from all sections were combined, and the benzene layer was separated from the aqueous-methanol layer. The benzene layer was washed three times with distilled water to remove the methanol, then the combined aqueous portion was back extracted with three small portions of benzene to recover any oil from the washings. The final benzene extract was found to weigh 2123 grams and to contain approximately 46 grams of solvent-free oil. This benzene solution of extracted oil was distributed to participating laboratories for subsequent analysis as indicated in Figure 1 (Section 1).

Quantities of Materials

The combined weight of core material used for extraction was 1581 grams. The weight of dry core material

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[1] These reports were prepared by the participating laboratories. Numbers in parentheses refer back to the appropriate part of Section 1 of this chapter.

recovered after extraction was 1384 grams giving a weight loss of 197 grams which must have represented the sum of oil, water and mechanical loss. Since the later was believed to be small, the total loss less the weight of oil recovered (46 grams) indicated that approximately 151 grams of water were present in the core material when extracted.

2.2 ROCK DESCRIPTIONS OF CORES 5 AND 6 (1.3)

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Shell Development Company, Houston, Texas

Rock Description, Core 5, Challenger Knoll

Gross Character

The core was composed of about five feet (1.5 m) of a friable assemblage of sand-sized, calcite crystals, with a significant content of sulfur crystals in the basal one-third of the core. A heavy tarry oil impregnated the upper two-thirds of the core.

Much of the core was slabbed with a palette knife; the core had a texture and consistency of wet, coarse sand, and had a few thin, lightly lithified zones. A single 2-1/2 inch (6.3 cm) zone within the oil impregnated two-thirds of the core was sufficiently lithified to be self-supporting and was impregnated and prepared as a plastic mount.

Thin Sections

Thin sections of the lithified zone show the core to be a rather pure calcite, with frequent inclusions of oil in cracks and crystal zones. Sulfur is commonly distributed in former voids between calcite crystals. The over-all texture of the rock is of a loosely interlocking mass of calcite crystals with little or no cementation evident; triangular cross sections of scalenohedral calcite crystals are commonly observed. Luminescent photomicrographs demonstrate several subtle varieties of calcite.

Chemical Composition

A series of samples were collected every 7 to 8 centimeters from the extracted cores for insoluble residue and spectrochemical analysis. Rock material is grossly composed of about 97 per cent calcite and about 3 per cent unidentified organic matter. Spectrochemical survey analysis indicates an average composition of calcium 35 per cent, silicon 0.9 per cent, manganese 0.1 per cent, magnesium 1 per cent, iron 0.7 per cent, and strontium 0.02 per cent.

Isotope Analysis

(R. M. Lloyd, Shell Development Company, EPRC)

A small portion of the core was ground off with special effort to sample only carbonate and avoid the areas of sulfur. X-ray analysis of the powder shows only calcite to be present. The sample was prepared by standard methods and the following isotope values (relative to the PDB-I standard) were determined:

δO^{18} + 0.05°/oo

δC^{13} - 25.30°/oo

The carbon value is unusually negative, suggesting the incorporation of carbon derived from the oxidation of organic material (possibly hydrocarbon). The oxygen value is equivalent to what would be expected of calcite precipitated in equilibrium with ocean water at a temperature of about 16°C.

Insoluble Residue

See Section 2.3

Rock Description, Core 6, Challenger Knoll

Gross Character

Core 6 consisted of a handful of egg-sized, well-lithified gypsum nodules and fragments.

Thin Sections and Chemical Analysis

Thin sections and chemical analysis of one of the fragments demonstrates it to be composed of rather pure gypsum; spectrochemical analysis indicates calcium 25 per cent, and magnesium 0.3 per cent.

2.3 PETROLOGY AND PALYNOLOGY OF CORES 5 AND 6, CHALLENGER KNOLL, GULF OF MEXICO (1.3.1)

D. W. Kirkland,
Mobil Field Research Laboratory, Dallas, Texas

Introduction

This report is based on a study of the petrology and palynology of Cores 5 and 6 from Site 2 of Leg 1, Deep Sea Drilling Project. The cores were recovered during the period from August 17 through 19, 1968 from the Challenger Knoll, one of many low hills protruding above the otherwise flat floor of the central part of the Gulf of Mexico.

Core 5 was taken from 447 to 454 feet (136.2-138.4 m) beneath the sediment surface (12,200 to 12,207 feet (3718.6-3720.7 m) beneath the drilling table); 6.5 feet (1.97 m) of core were recovered. The upper part of the core was saturated with oil. In order to avoid contaminating the lower part, the core was divided on shipboard into an upper part designated 5-1 and a lower part designated 5-2. Core 6 was taken 8 feet (2.44 m) below the base of Core 5, from 462 to 472 feet (140.8 to 143.9 m) beneath the sediment surface (12,215 to 12,225 feet (3723.1-3726.2 m) beneath the drilling table); only about 1 foot (30.5 cm) of core was recovered.

Core 5 was opened at the Field Research Laboratory of Mobil Research and Development Corporation, Dallas, Texas, on October 10, 1968. The core had been reduced in length by about one third, since measurement on shipboard, apparently because of compaction during transportation and handling.

Core 5-1, 2.83 feet (86.2 cm) in length, consists principally of oil-coated fragments of calcite. The fragments are loose and generally less than 0.5 centimeters; only a few larger pieces (up to about 3.5 centimeters) are present. Stratigraphic continuity was assumed, and longitudinal half-sections of the core were removed in approximately 3-inch (7.6 cm) intervals for petrographic analysis. Core 5-2, 1.5 feet (45.8 cm) in length, consists principally of loose crystal fragments of sulfur and calcite. Several pieces have dimensions up to approximately 4 centimeters, but most fragments are less than 0.5 centimeter. Stratigraphic continuity was not assumed, because it appeared that the core material could easily have been mixed. A very thin film of oil, which cannot be seen easily, coats the fragments. Plate 1, of Section 1, shows the archive half of Cores 5-1 and 5-2 in plastic D-tubes.

Core 6 consists of several samples, about 3 to 4 centimeters in diameter, principally of oil-stained gypsum.

The writer acknowledges the help of A.B. Spencer, who did the X-ray analyses, R.F. Sippel, who did the luminescence petrography, and J.E. Gerhard and N.O. Frederiksen, who helped identify palynomorphs. E.G. Wermund read the manuscript and offered constructive criticism.

Petrology

The weakly adhering and brittle rock mass represented by Core 5 was broken into numerous fragments during coring (e.g. Plate 2A and B). It consisted of gray, finely-crystalline, pyritic calcite veins bounded by brownish white, coarser calcite and numerous vugs. In the lower third, the vugs were generally, partially or totally filled with sulfur crystals. The rock mass represented by Core 6 consisted mainly of essentially non-porous gypsum.

The major minerals in Cores 5 and 6, which comprise 98 per cent or more of the rock, are calcite, sulfur and gypsum. Their paragenesis is apparent. Calcite and sulfur replace and fill the vugs in gypsum and are clearly younger minerals. Sulfur is undoubtedly the last mineral to have formed.

The characteristics and mode of occurrence of minerals identified in the cores follows.

Calcite

Calcite constitutes about 98 per cent of the mineral matter in Core 5-1, and about 80 per cent in Core 5-2. Megascopically, fragments of calcite from Core 5 can be classified as light- or dark-colored. Overall, Core 5-1 is composed of about 60 per cent light- and 40 per cent dark-colored calcite. The proportion of these rock types varies vertically. The intervals, 20 to 23 inches and 28 to 31 inches (51-58.5 and 71.2-76.3 cm) above the base of the core, are particularly high in light-colored calcite (approximately 85 per cent). The calcite portion of Core 5-2 consists of about 35 per cent dark- and 65 per cent light-colored calcite. Most calcite fragments are either brownish white or medium to dark gray. The gray color is due chiefly to small, finely disseminated pyrite crystals. The pyritic calcite is finely crystalline. Plate 3 shows a vein of pyritic calcite bordered by light-colored calcite and sulfur.

The calcite crystals bounding vugs and sulfur masses in Core 5 are commonly scalenohedrons (Plates 4, A-D and 5), a habit typical of secondary calcite. Crystals of this type grow in cavities, and their great abundance attests to the original high porosity of the section cored. Calcite also commonly forms a mosaic of interlocking anhedral crystals (Plate 6 and 7); crystal size varies considerably in different parts of the core with "pockets" of coarser crystalline calcite occurring in a finer calcite mosaic.

Calcite replaces and fills voids in gypsum, and in Core 5-2 sulfur sometimes replaces calcite (e.g. Plate 8).

During calcite crystallization, the physical-chemical environment varied sufficiently to cause zoning. One type of calcite zoning encountered rarely in thin sections of Core 5-1 consists of a triangular void in the center of a scalenohedron, or a thin void which parallels and is just inside the crystal margin (Plate 9A and B). The material which occupied these voids has apparently been selectively leached because of a compositional difference.

Zoning, although probably common in calcite, is seldom detected without special methods. Thin sections from Core 5 were examined microscopically by luminescent light. Most of the calcite luminesces in blue shades. Some calcite adjacent to voids shows an outer orange rim (Plate 10C). Luminescing calcite is also sparsely present along some pyrite veins. The orange luminescing calcite is apparently a late generation of calcite containing relatively larger, although still only trace amounts, of manganese; it apparently postdates sulfur deposition. Spectro-chemical analysis indicates an average manganese content in Core 5-1 of about 0.1 per cent. Also, water from Core 5 had a high content of manganese (more than 100 ppm).

Sulfur

Sulfur comprises about 19 per cent by weight of the rock mass in Core 5-2. Sulfur was not observed in

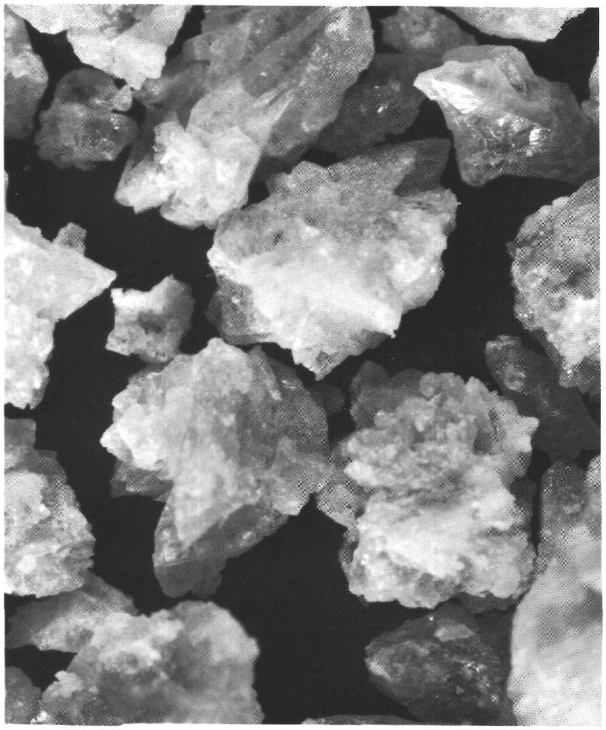


Plate 2A. *Calcite crystal aggregates from unconsolidated part of Core 5-1, 28-31 inches (71.3-79 cm) above base;* × *14.*

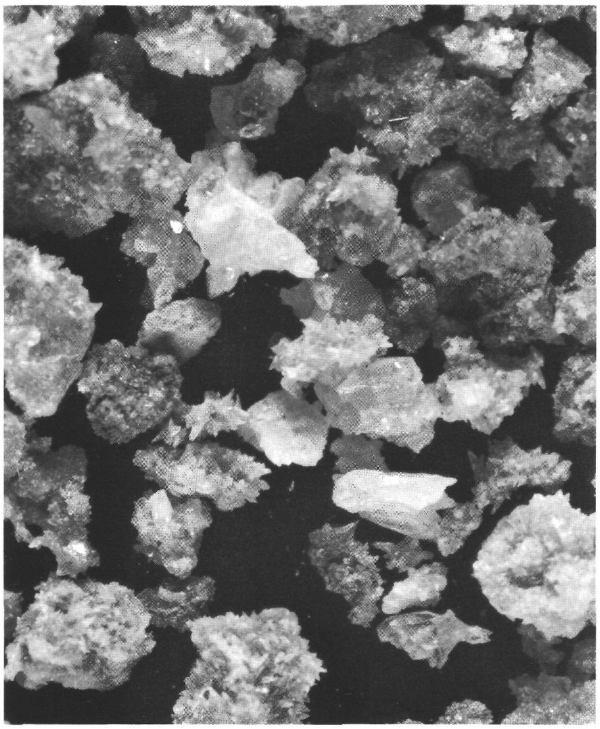


Plate 2B. *Calcite crystal aggregates from unconsolidated part of Core 5-1, 0-3 inches (0-7.6 cm) above base;* × *14.*

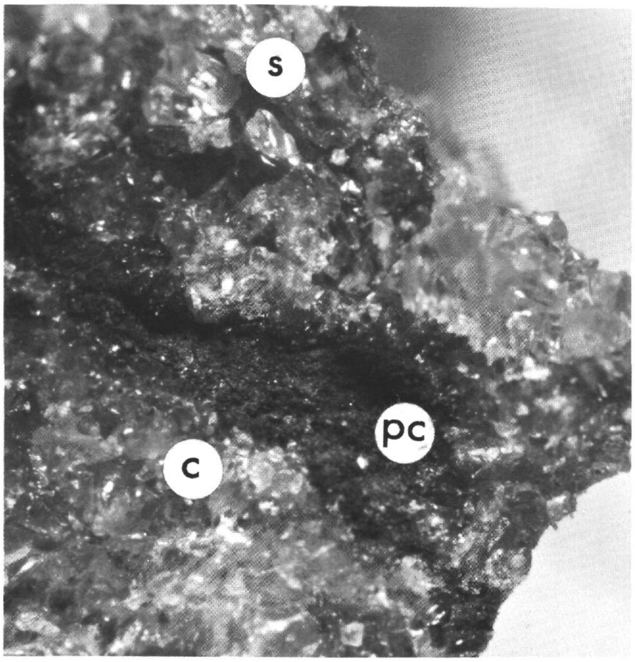


Plate 3. *Vein of pyritic calcite (pc); comparatively large, light-colored crystals of calcite (c) border the vein; sulfur (s) borders the calcite; Core 5-2,* × *22.*

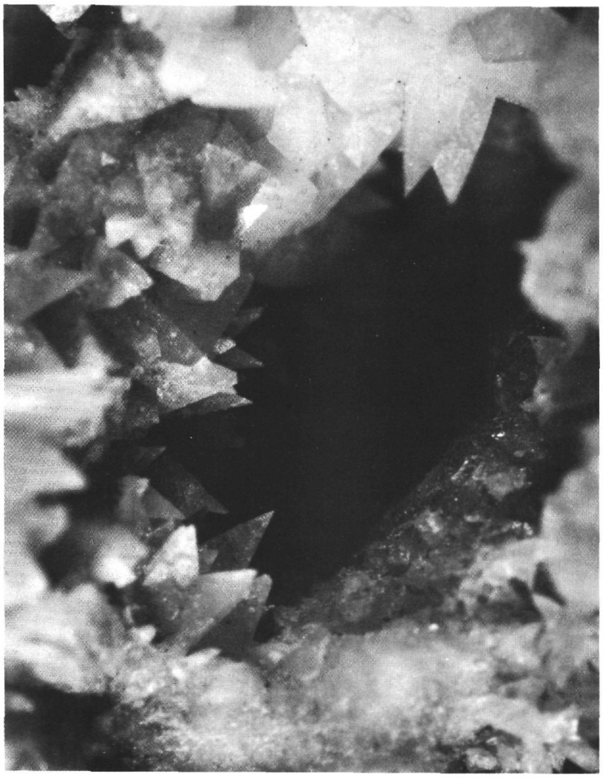


Plate 4A. *Euhedral crystals of calcite surrounding a vug; Core 5-1, 28-31 inches (71.3-79 cm) above base;* × *22.*

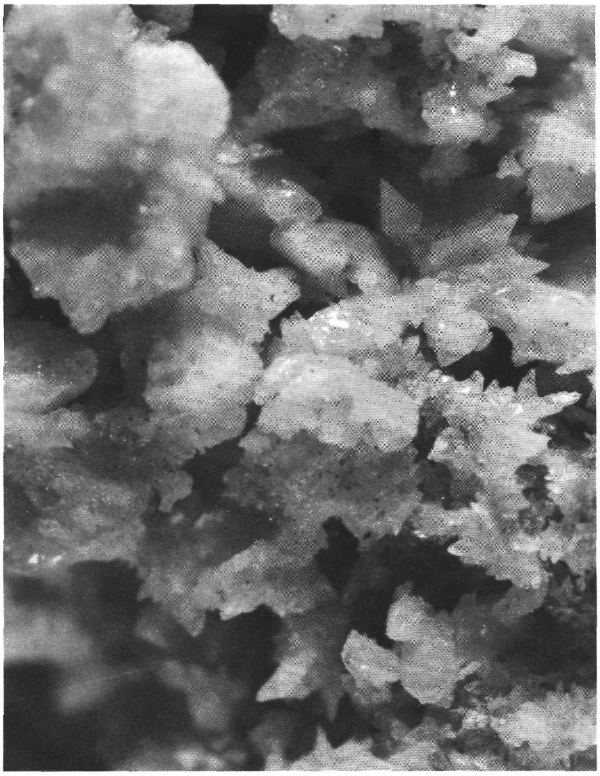


Plate 4B. *Scalenohedral calcite crystals; Core 5-1, 3-5 inches (7.6-12.7 cm) above base;* × *22.*

Plate 4C. *Dark gray calcite crystals from Core 5-1,* × *300, (photomicrograph taken with scanning electron microscope).*

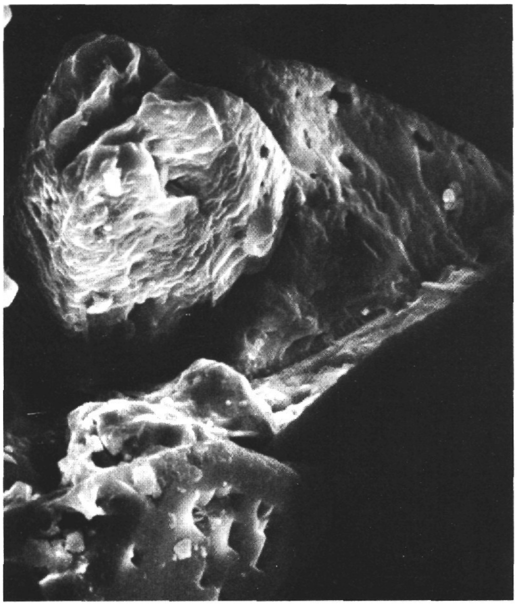


Plate 4D. *Portion of several crystals illustrated in 4C;* × *1000; note the small pores on the crystal faces (photomicrograph taken with scanning electron microscope).*

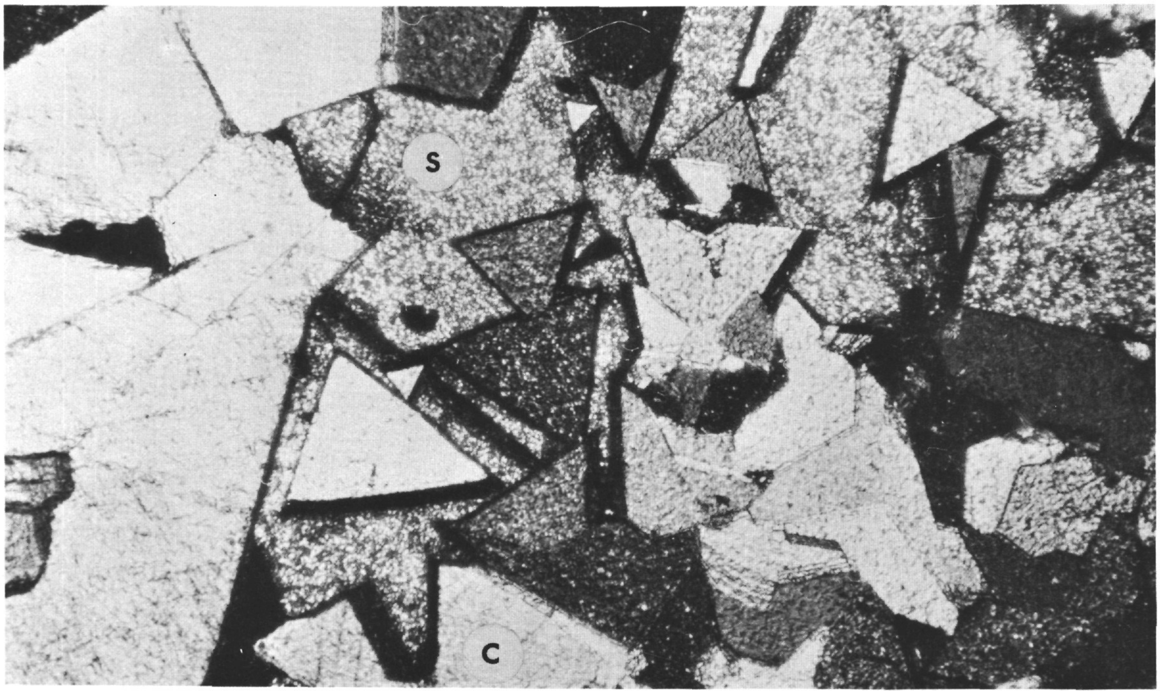


Plate 5. *Calcite scalenohedrons in sulfur, Core 5-2, 23 inches (58.6 cm) above base; c, calcite; s, sulfur; Nichols crossed;* × *80.*

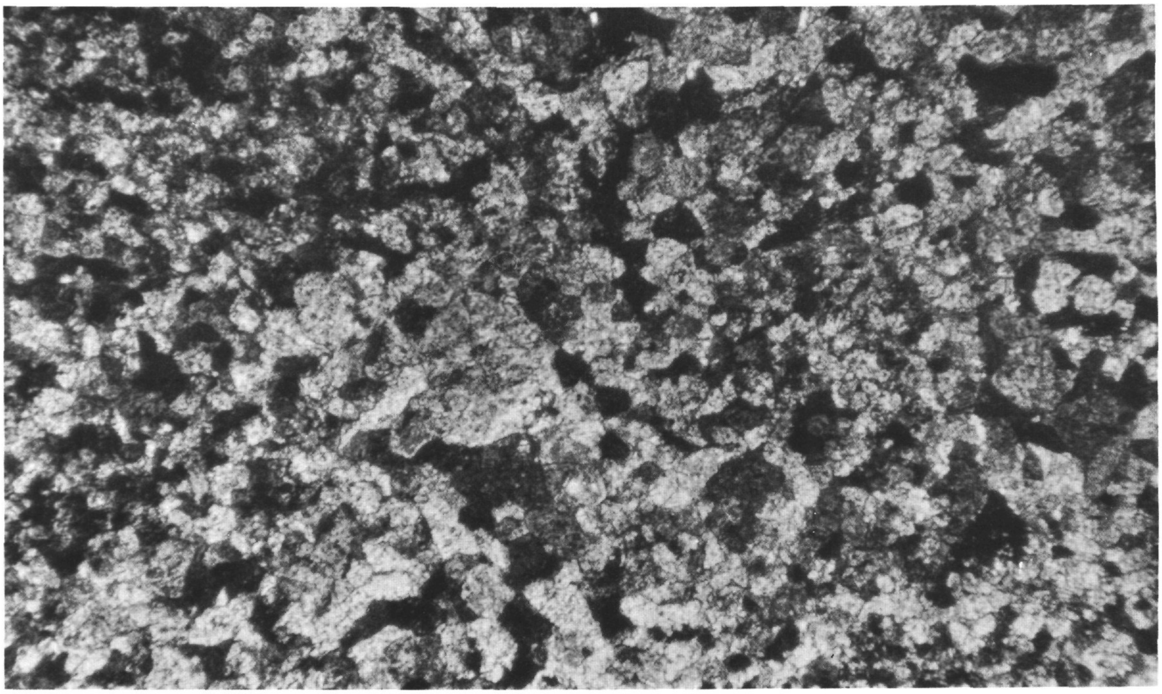


Plate 6. *Calcite crystal mosaic, Core 5-2, 1.5 inches (3.6 cm) above base; Nichols crossed;* × *80.*

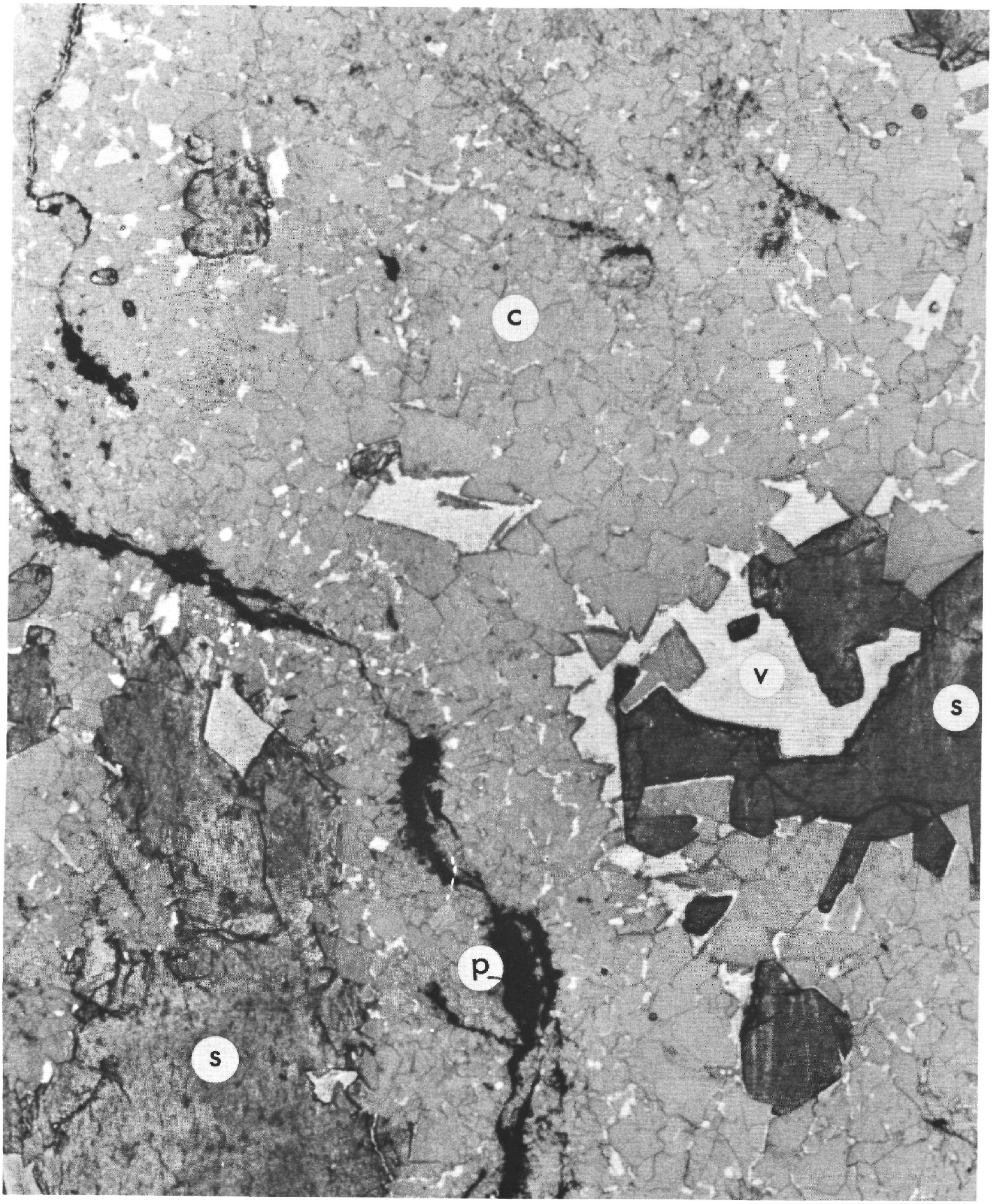


Plate 7. *Sulfur crystals in calcite mosaic, Core 5-2, 23 inches (58.6 cm) above base; s, sulfur; c, calcite; p, pyrite; v, void; plain light;* × *22.*

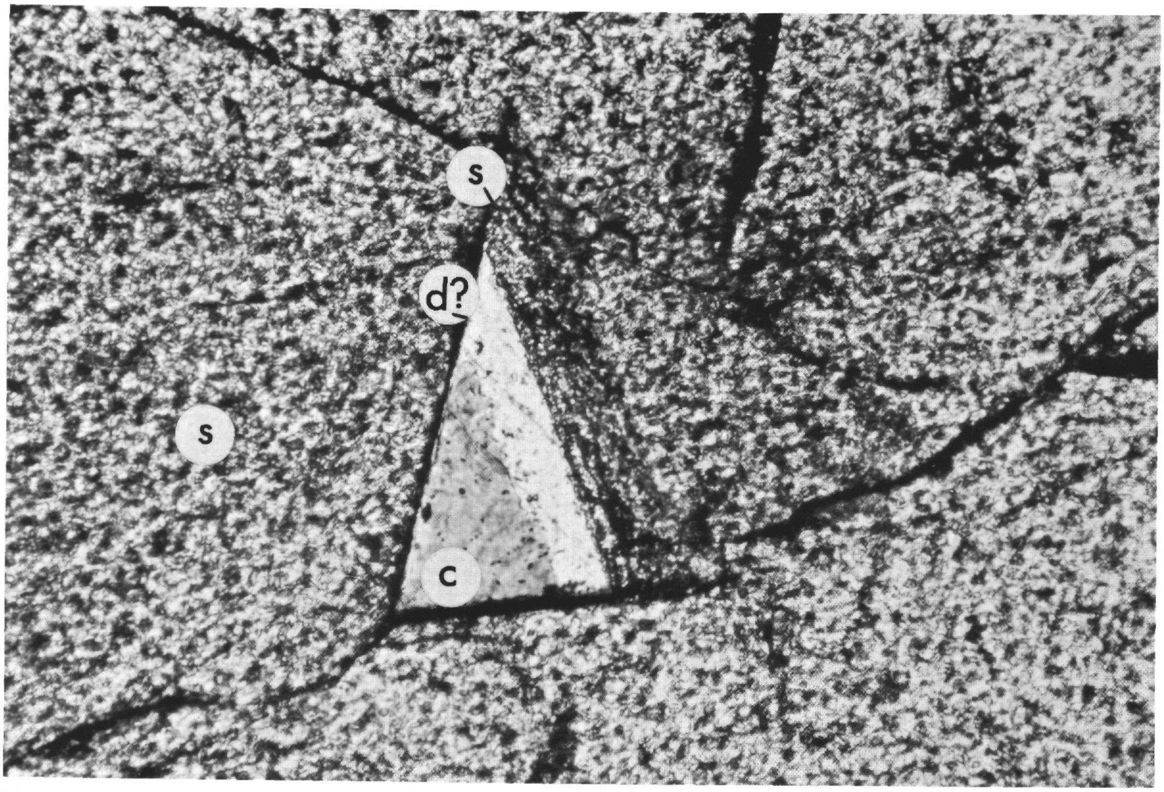


Plate 8. *Calcite scalenohedron in sulfur, Core 5-2, 23 inches (58.6 cm) above base; calcite (c) is partially replaced by dolomite (?) (d?) and sulfur (s), plain light;* × *236.*

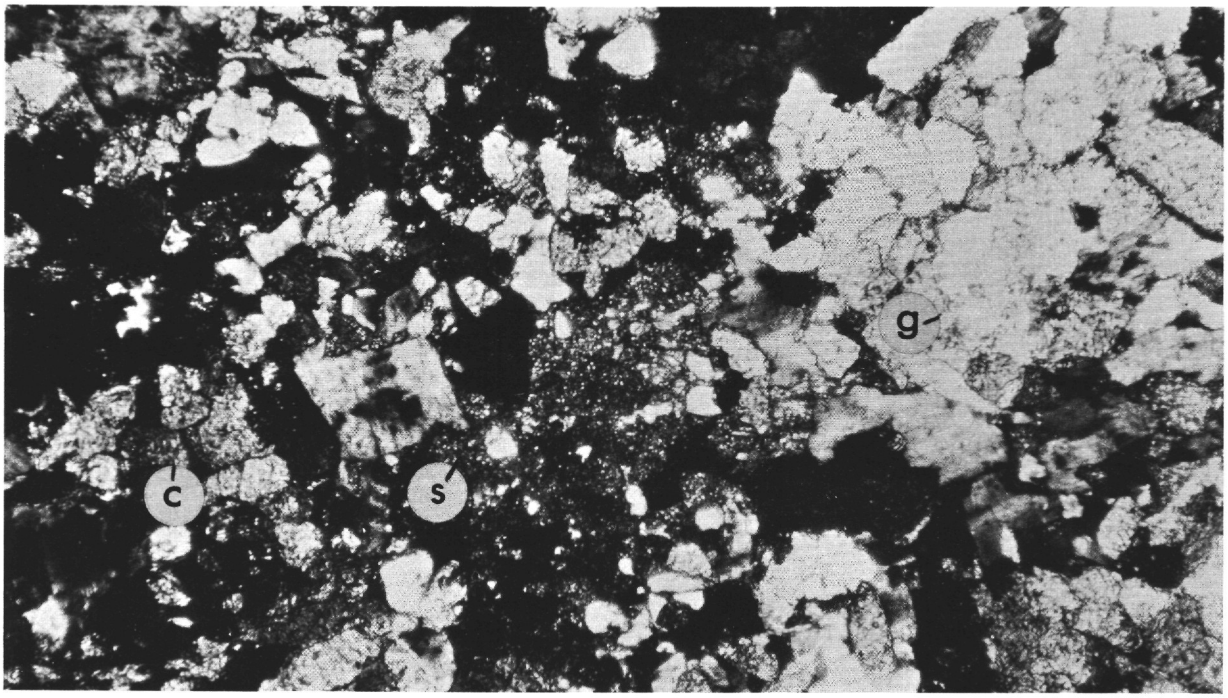


Plate 9A. *Sulfur crystals with calcite and gypsum; Core 6; s, sulfur; c, calcite; g, gypsum; Nichols crossed;* × *80.*

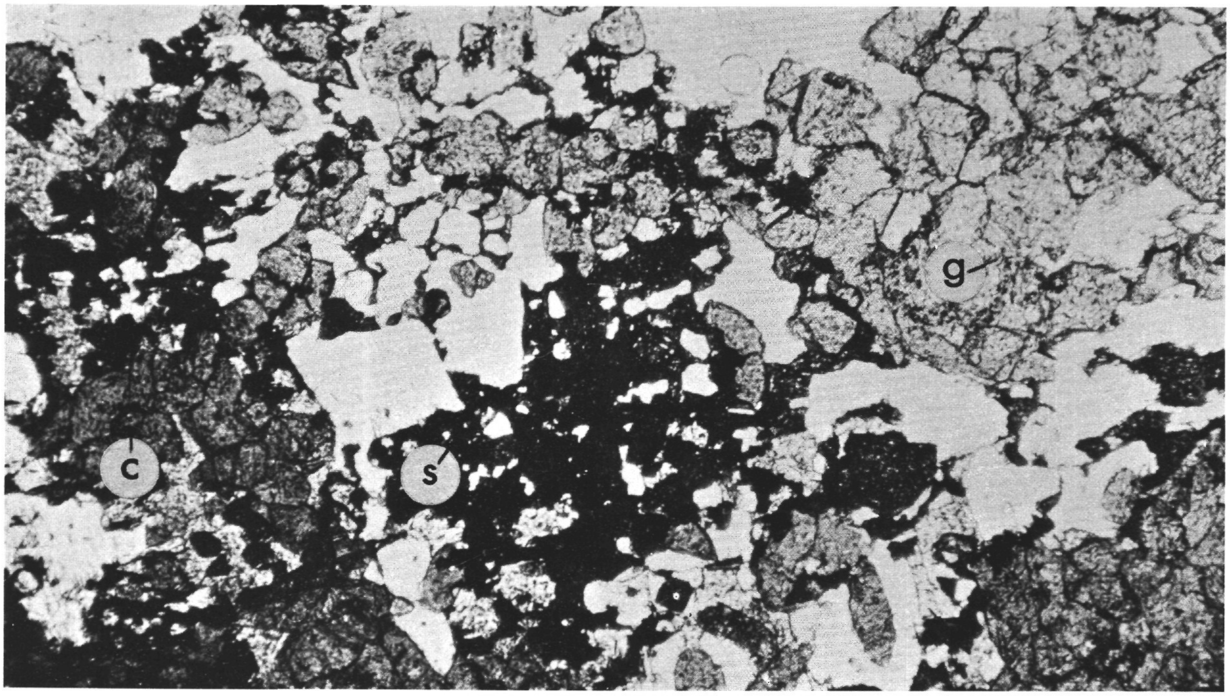


Plate 9B. *Sulfur crystals with calcite and gypsum; Core 6; same view as Plate 9A; plain light;* × *80.*

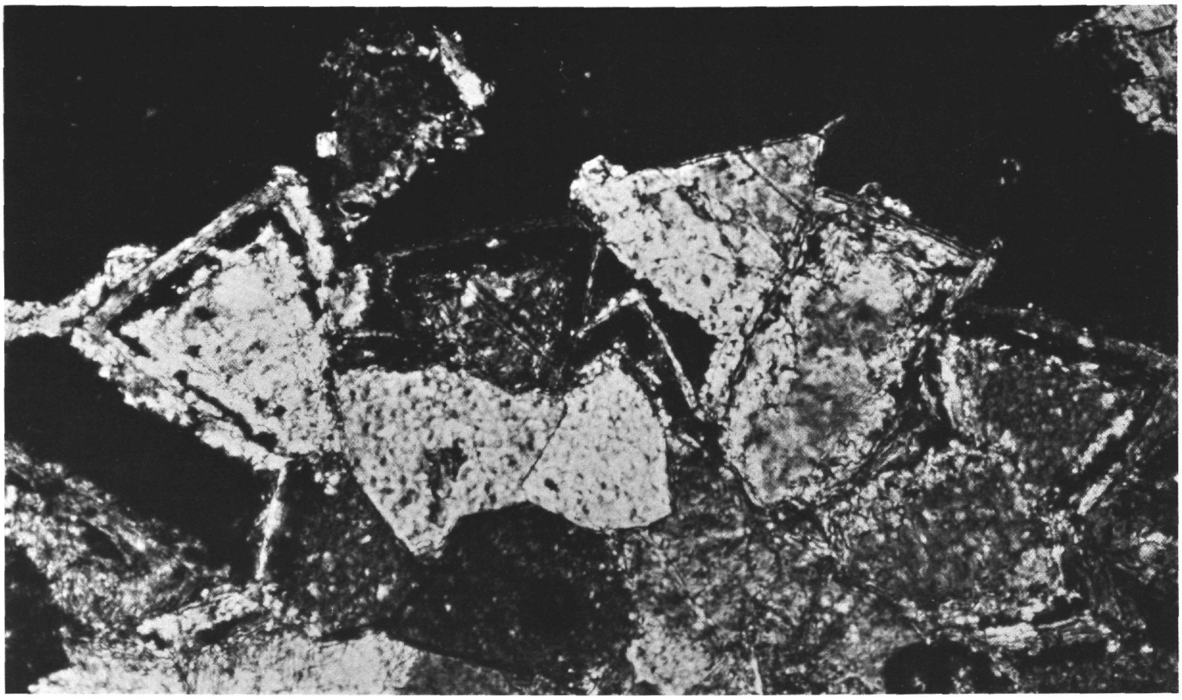


Plate 10A. *Zoning in calcite scalenohedrons; Core 5-2, 11 1/2 inches (28.3 cm) above base of core; Nichols crossed;* × *236.*

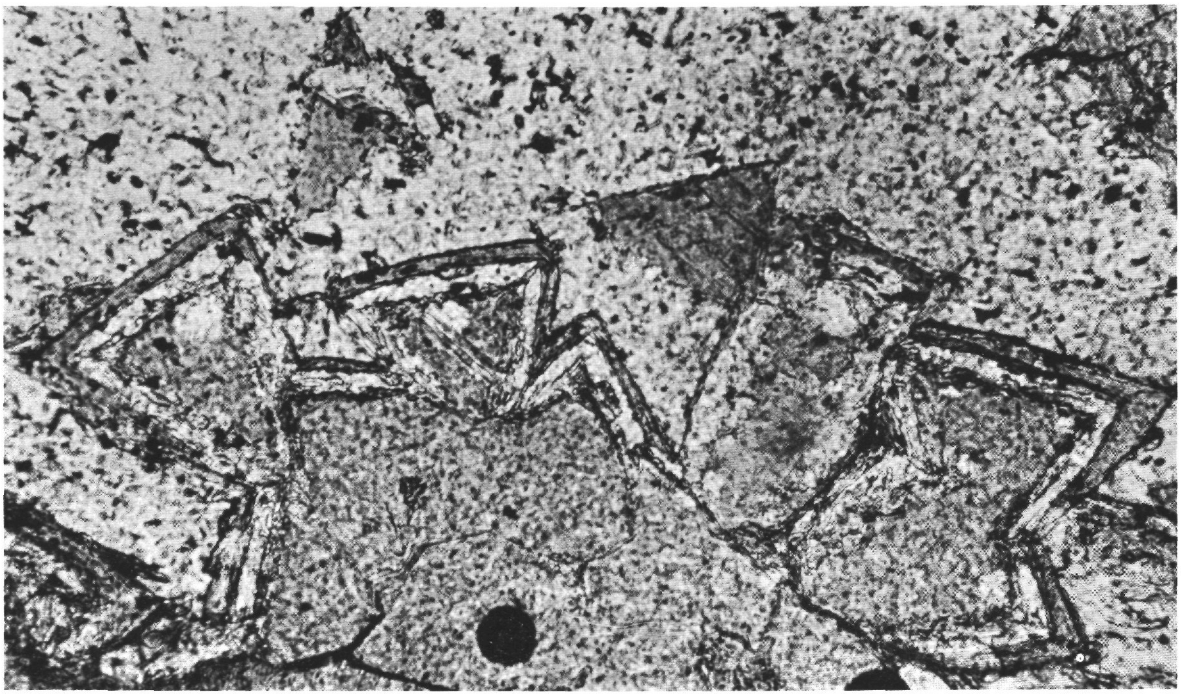


Plate 10B. *Zoning in calcite scalenohedrons; same view as 10A; plain light;* × *236.*

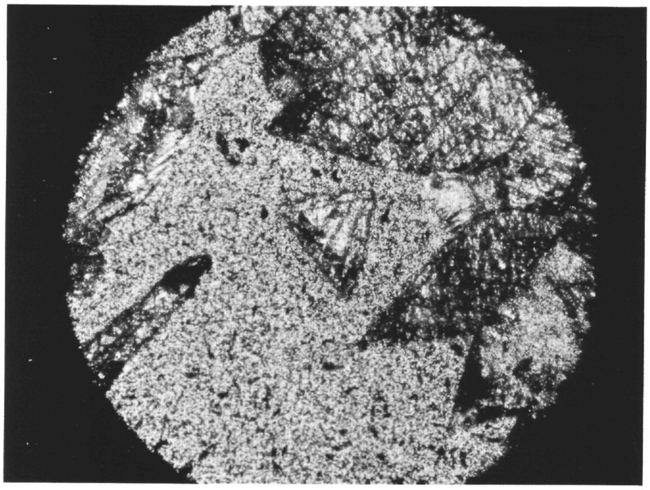


Plate 11A. *Calcite crystals in plain light; Core 5-1;* × *44.*

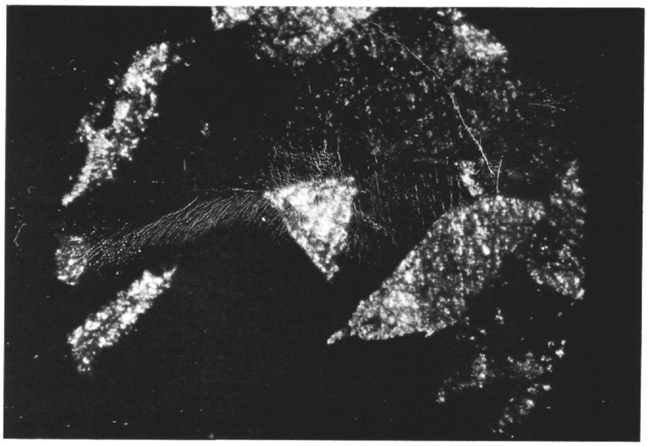


Plate 11B. *Calcite crystals in polarized light, Core 5-1; same view as 11A;* × *44.*

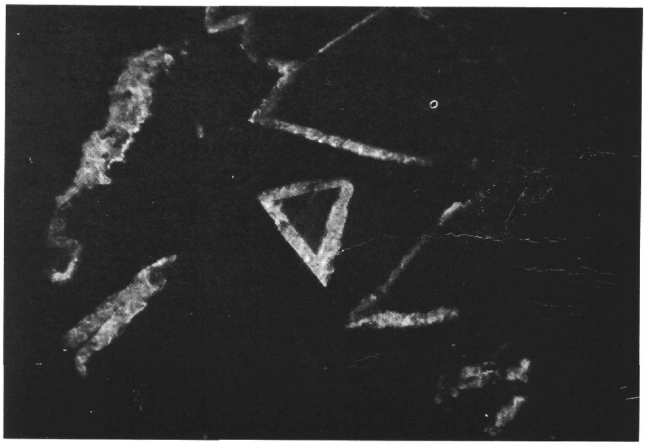


Plate 11C. *Calcite crystals in luminescent light; Core 5-1; same view as 11A;* × *44.*

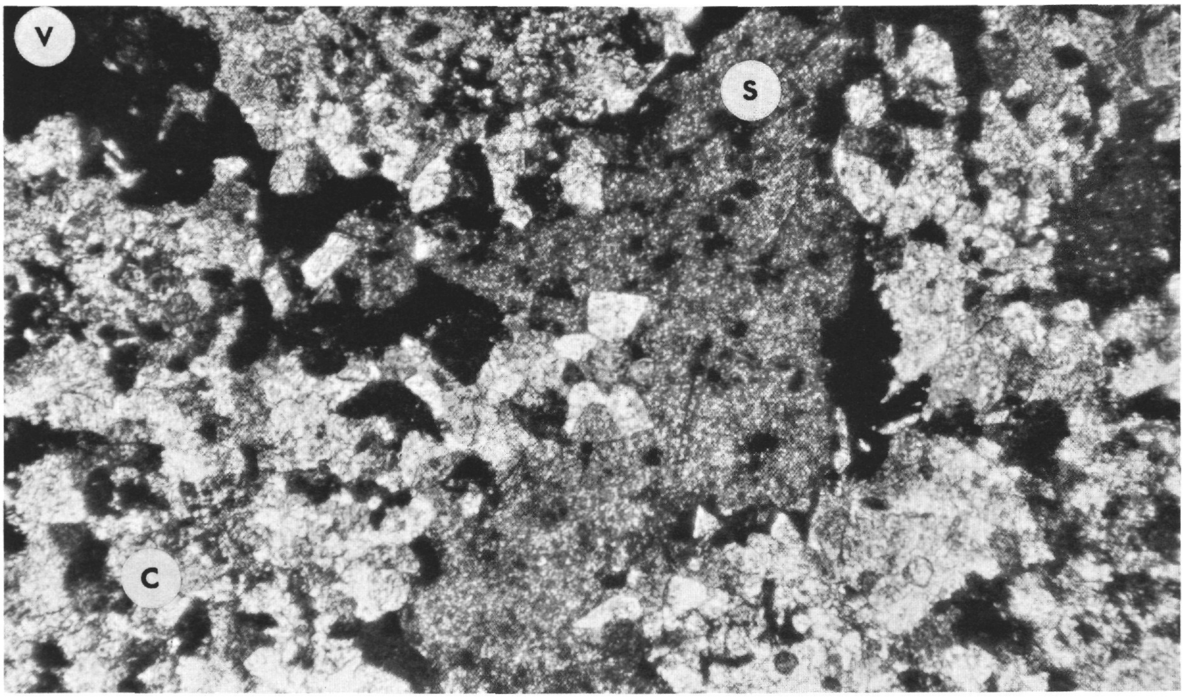


Plate 12A. *Sulfur (s) crystal in calcite (c); v, void; Nichols crossed;* × *80.*

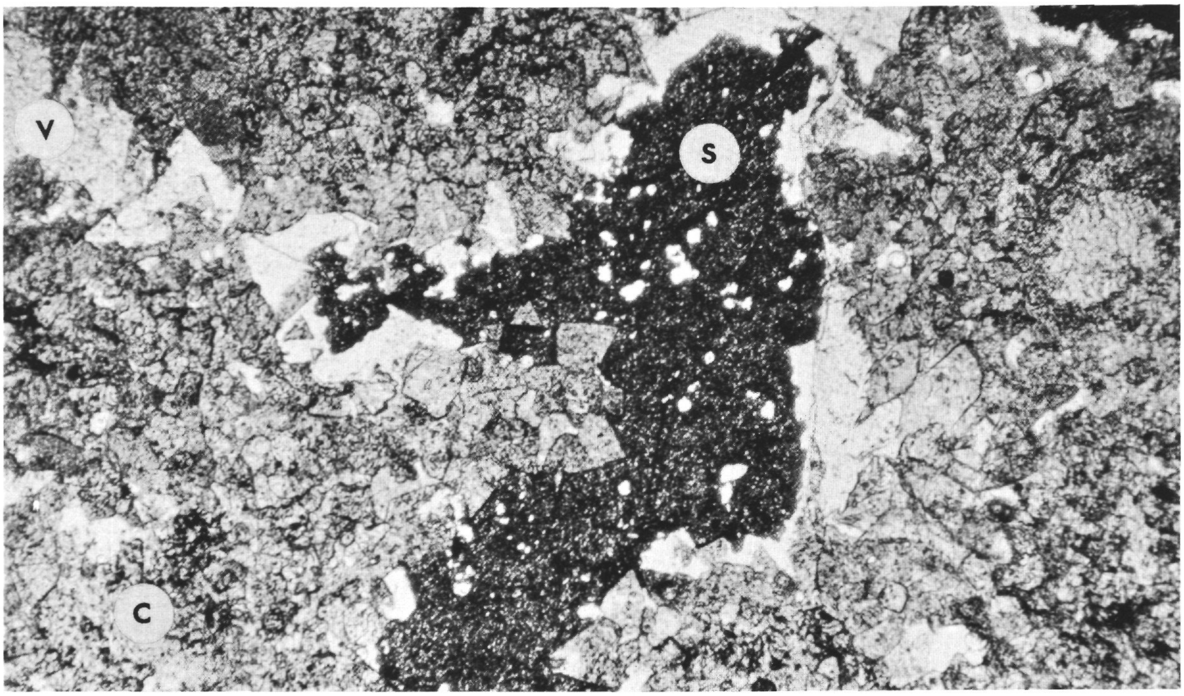


Plate 12B. *Sulfur crystal in calcite; same view as Plate 12A; plain light;* × *80.*

Core 5-1, but constitutes a minor amount (less than 1 per cent) of Core 6. Most sulfur from Core 5-2 occurs as bright yellow crystal fragments less than 0.5 centimeter in maximum dimension. Sulfur crystals larger than 1 centimeter were rare. Some crystals occur as subhedral "truncated pyramids" or with well developed crystal faces, indicating formation in a cavity. Most sulfur in Core 5-2 occurs as vug-fillings in a calcite matrix (Plates 7, 11A and B and 12A and B). Replacement of calcite and gypsum by sulfur was only rarely observed.

Sulfur is present in Core 5-2, but absent from overlying Core 5-1 and, whereas, the oil content of Core 5-1 is high, that of underlying Core 5-2 is very low. Possibly, the contact between the sulfur-bearing calcite (Core 5-2) and the overlying oil-bearing calcite (Core 5-1) represents an oil-water contact with sulfur deposition restricted to the water phase.

Gypsum

Core 6 consists predominately of a mosaic of randomly-oriented, equant gypsum crystals generally less than 0.5 millimeter in maximum dimension (Plate 13B). The crystal boundaries are sometimes sutured, and are roughly straight-sided. Calcite and more rarely pyrite veins are deposited along some gypsum crystal boundaries (Plate 13A). Calcite, rarely dolomite (?) and sulfur replace the gypsum. Anhydrite was not observed.

Pyrite

Pyrite constitutes about 0.50 per cent of Core 5 and occurs in veins (Plates 7 and 14A and B) and as small micron-size crystals disseminated in calcite. Pyrite was identified microscopically and by X-ray analysis of the residue remaining after the solution of gray calcite in 6 normal hydrochloric acid. Pyritohedrons with a maximum dimension of about 0.1 millimeter were rarely observed in the insoluble residue fraction. Pyrite veins in thin section are difficult to distinguish from veins of organic residue, but the metalic luster, crystal faces, and brass-yellow color of pyrite can be seen readily in reflected light at 160 X magnification. The pyrite veins do not cross sulfur crystals and are not interrupted by vugs.

Quartz

Quartz constitutes approximately 0.20 per cent of Core 5. Three types were observed in insoluble residues of Core 5: (1) well-formed hexagonal prisms with two equally developed rhombohedrons (Plate 15), (2) "rosettes", in which singly terminated crystals radiate from a center (Plates 16, 18 and 19), and (3) rounded quartz, which may be silt grains (Plate 17).

Quartz crystals are apparently concentrated in gray calcite; they were not observed in sulfur masses not in gypsum. Rarely quartz (?) crystals could be observed within pyrite veins. Most of the quartz crystals are clear, but some single euhedral quartz prisms contain disseminated red material (hematite?), which can be seen best in plain light from the side.

Crystal mounts containing numerous specimens were studied by luminescence petrography. Single quartz crystals sometimes show faint blue luminescing centers which are probably detrital nuclei. Numerous rosettes were observed in which detrital nuclei were not definitely identified.

Quartz apparently does not replace other minerals present in the cores, and it is not replaced by them.

Tourmaline

Small, yellowish brown rhombohedrons of magnesium tourmaline (dravite) are present in Core 5 (Plate 20). Tourmaline constitutes 0.04 per cent by weight of Core 5-1, and 0.02 per cent of Core 5-2. The rhombohedrons range in size from 0.01 millimeter to 0.08 millimeter; most crystals are about 0.04 millimeter. The rhombohedral habit is dominant; however, prisms were rarely observed. Pleochroism is poorly exhibited in the rhombohedrons.

Authigenic tourmaline has been reported as overgrowths on detrital tourmaline (Pettijohn, 1957), however, the tourmaline rhombohedrons from Core 5 are not overgrowths on detrital fragments.

Tourmaline in Core 5 is probably confined to gray calcite. A single tourmaline crystal is shown in place in Plate 21 in dark-gray, pyritic calcite.

Tourmaline was confirmed by X-ray analysis. Lattice spacings characteristic of the variety dravite at 2.53 angstroms, 2.582 angstroms, 2.980 angstoms, 3.33 angstroms, 3.49 angstroms, 3.98 angstroms, 4.22 angstroms 5.00 angstroms and 6.40 angstroms were obtained.

Dolomite

Dolomite was detected by X-ray analysis of the residue remaining after dissolving a composite sample of Core 5-1 in 10 per cent acetic acid. Less than 0.5 (0.1 to 0.4) per cent magnesium is present in Core 5-1. Rhombohedrons of dolomite (?) were rarely observed in Core 6. Calcite crystals lining vugs in Core 5 often have a thin outer margin or rim which does not stain with alizarin red. This rimming mineral has simultaneous extinction with the central calcite crystal that it rims, and it also has high birefringence. It appears to be a carbonate–probably dolomite–and it does not luminesce.

Other Components

Approximately 50 ppm strontium is present in Core 5. This amount might be incorporated in the calcite

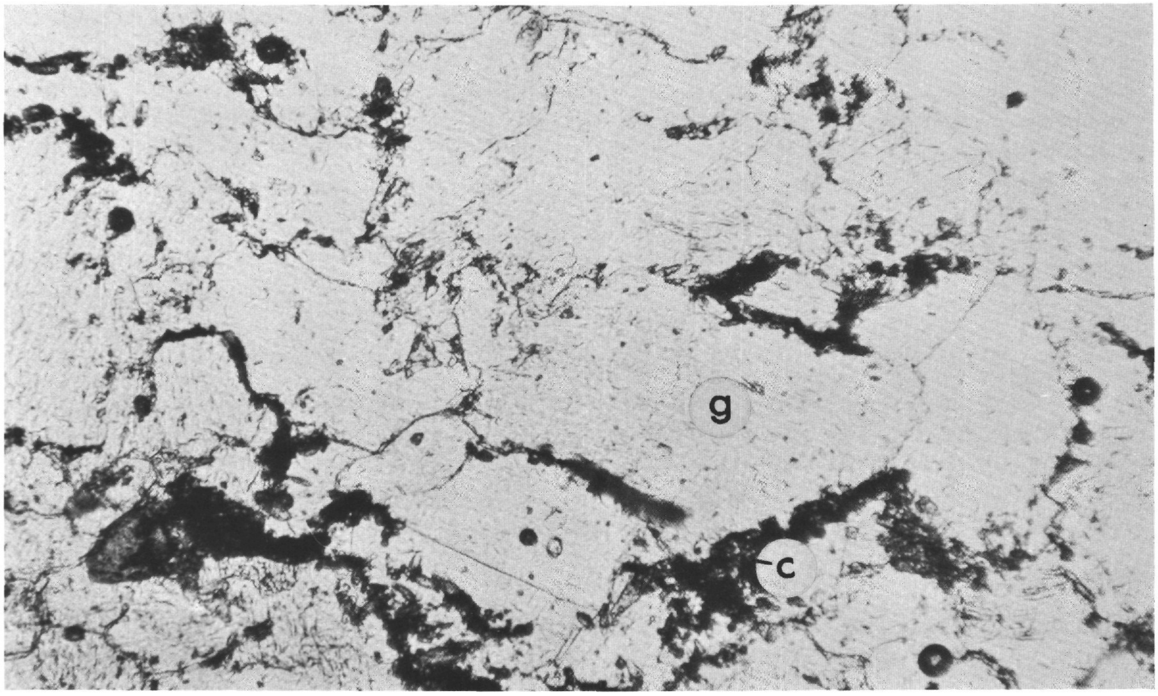


Plate 13A. *Gypsum crystal mosaic, Core 6; calcite (c) has been deposited along gypsum (g) crystal boundaries; plain light;* × *80.*

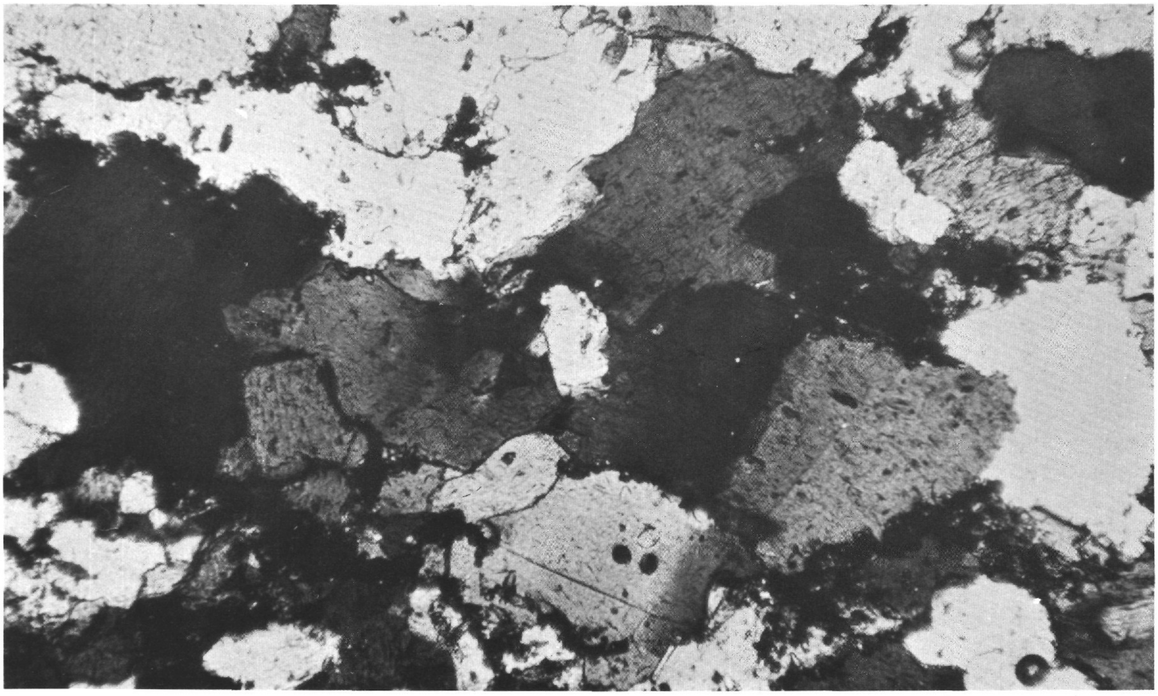


Plate 13B. *Gypsum crystal mosaic, Core 6; same view as Plate 13A; Nichols crossed;* × *80.*

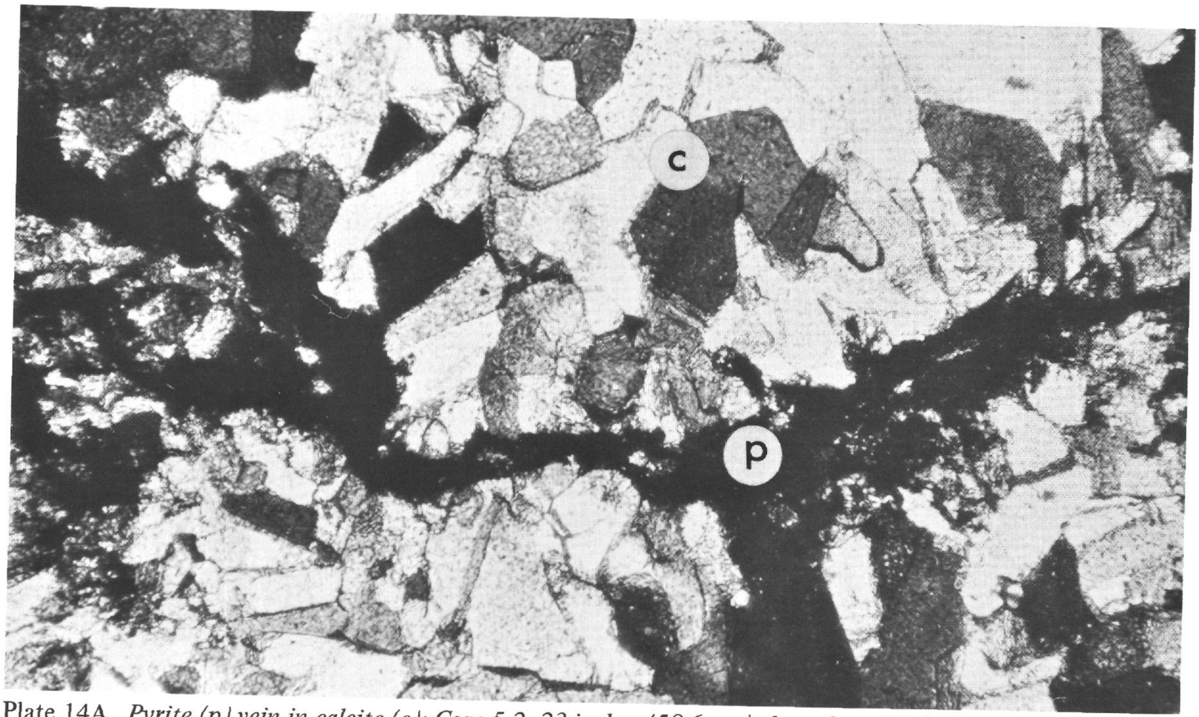


Plate 14A. *Pyrite (p) vein in calcite (c); Core 5-2, 23 inches (58.6 cm) above base; Nichols crossed;* × *80.*

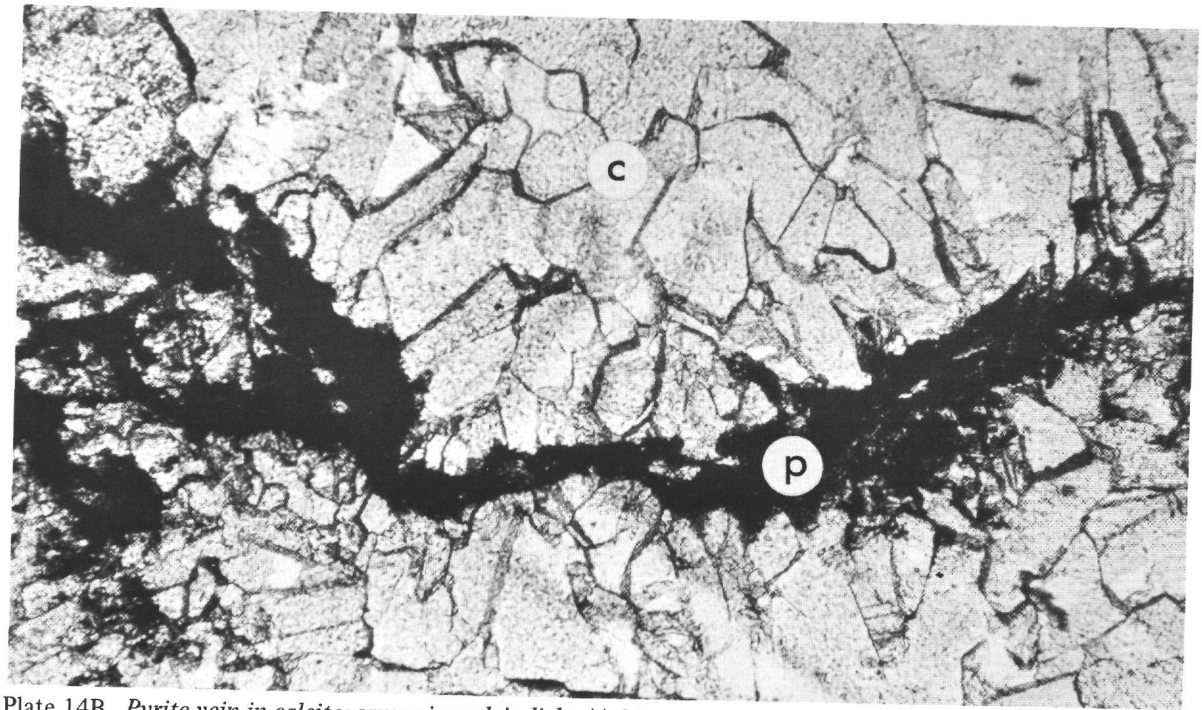


Plate 14B. *Pyrite vein in calcite; same view plain light;* × *80.*

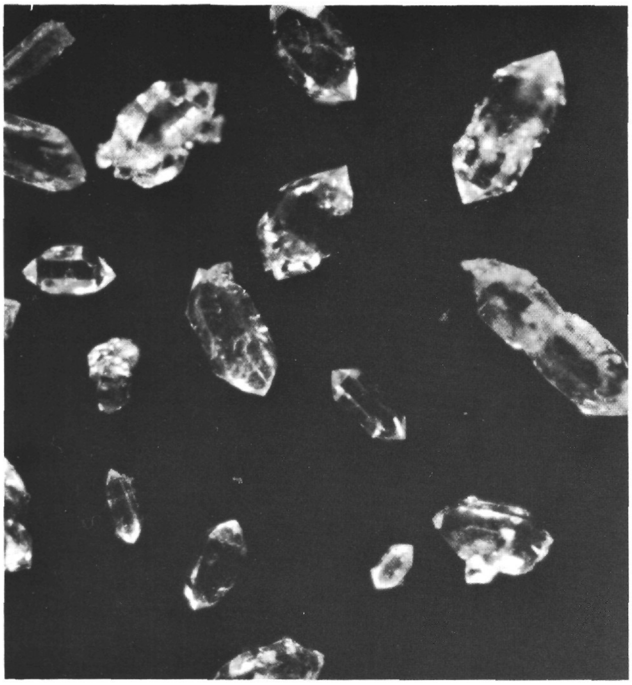


Plate 15. *Euhedral quartz crystals; portion of insoluble residue, Core 5-1 (composite sample); X 48.*

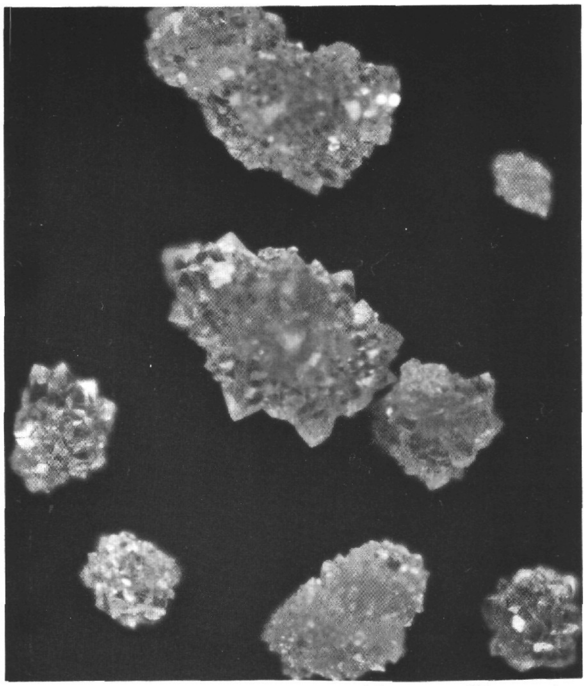


Plate 16. *Radial quartz clusters ("rosettes"); portion of insoluble residue. Core 5-1 (composite sample); X 48.*

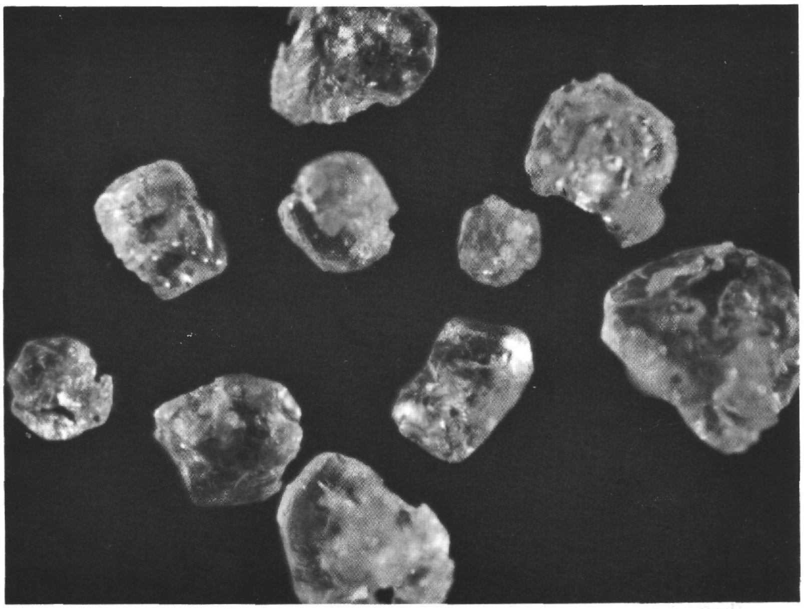


Plate 17. *Quartz grains; portion of insoluble residue, Core 5-1 (composite sample); X 48.*

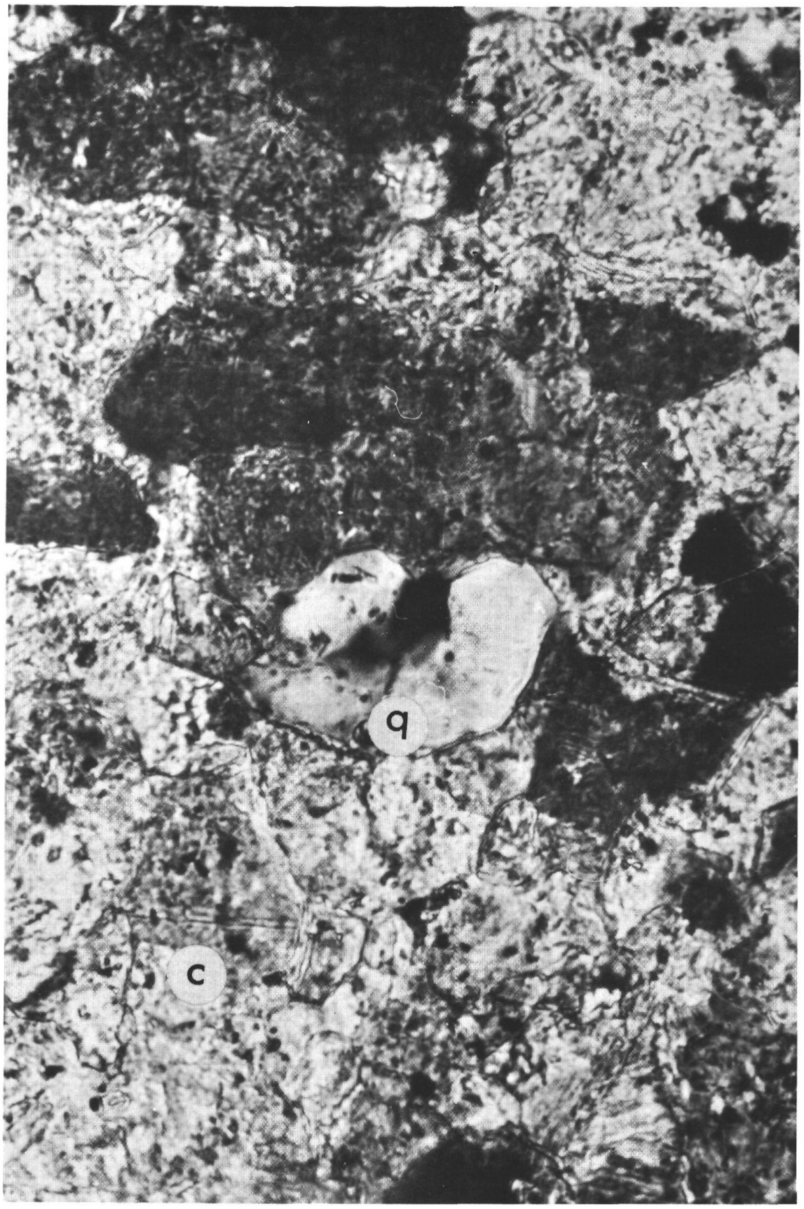


Plate 18. *Radial quartz cluster ("rosette") in calcite; Core 5-2, 11 1/2 inches (28.3 cm) above base; q, quartz; c, calcite; Nichols crossed;* × *585.*

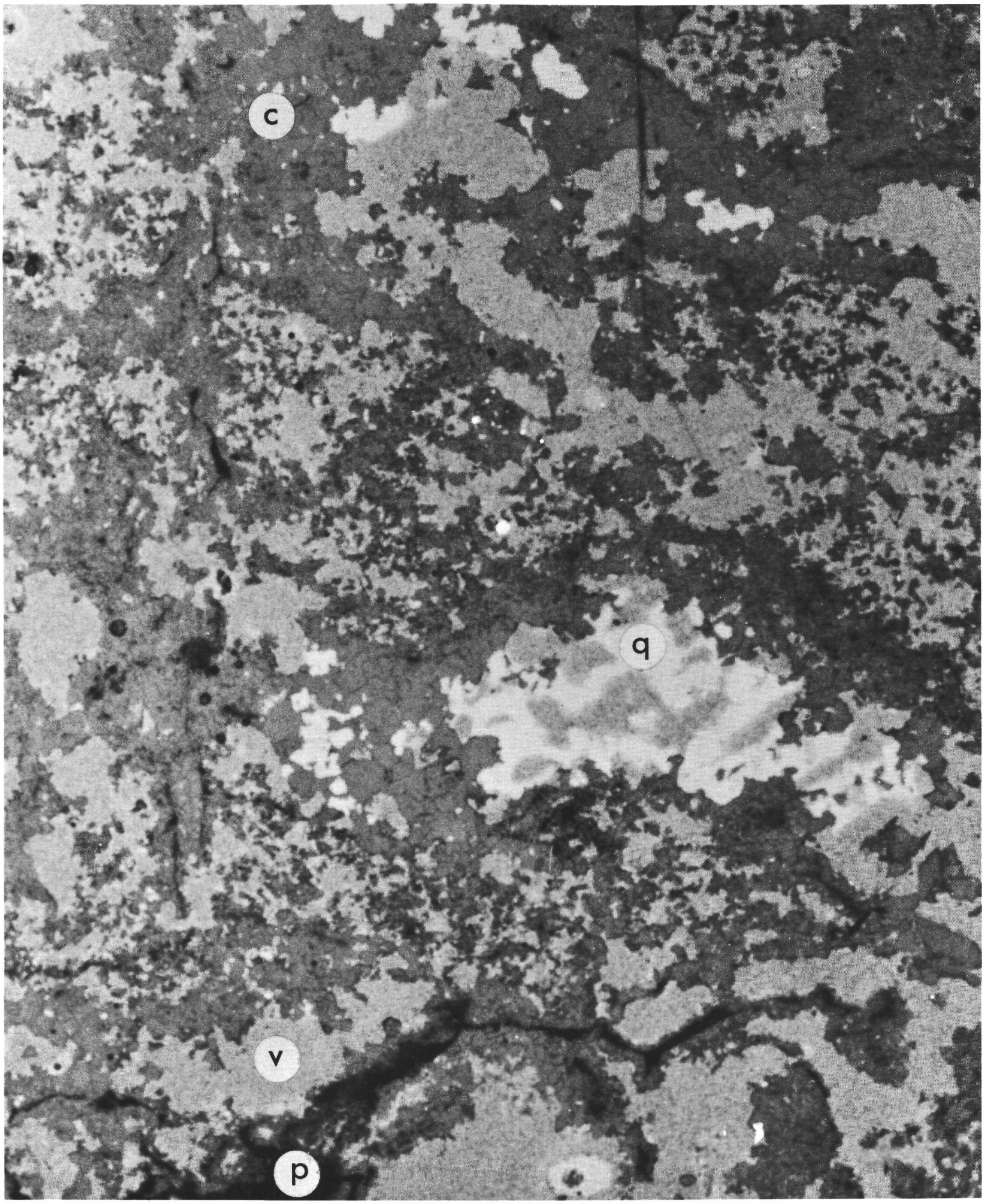


Plate 19. *Quartz crystal clusters in calcite; Core 5-1, 9-12 inches (22.9-30.5 cm) above base; q, quartz; c, calcite; v, void; p, pyrite; plain light;* × *22.*

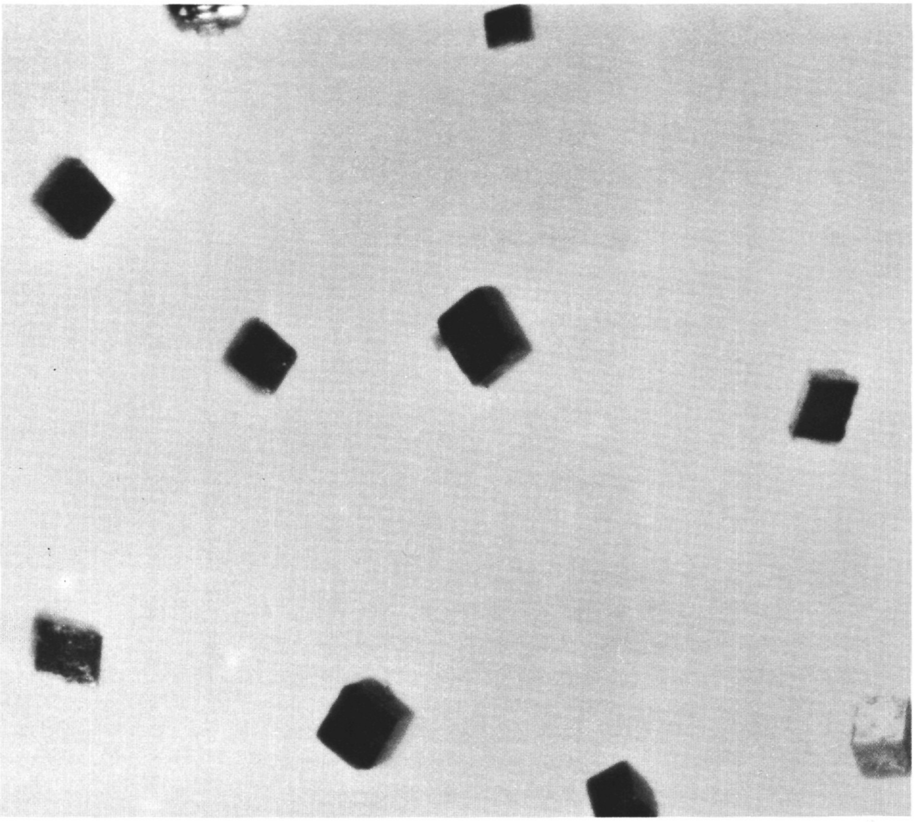


Plate 20. *Tourmaline crystals (rhombohedral habit) from portion of insoluble residue, Core 5-1 (composite sample);* × *100.*

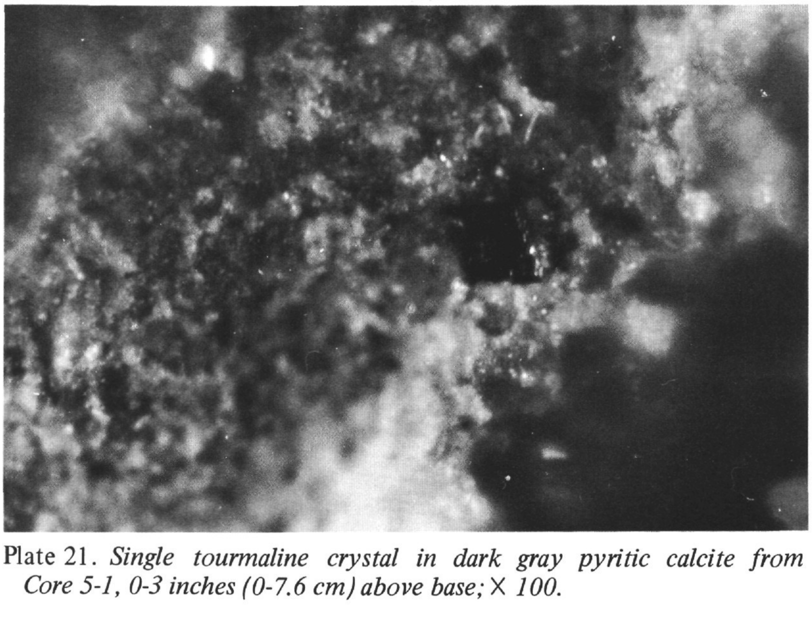


Plate 21. *Single tourmaline crystal in dark gray pyritic calcite from Core 5-1, 0-3 inches (0-7.6 cm) above base;* × *100.*

latice. Celestite ($SrSO_4$) or strontianite ($SrCO_3$) may be present, but these minerals were not observed in thin sections.

A small amount of the light fraction of insoluble residue from Core 5 (approximately 0.1 per cent) could not be identified with certainty, but it appears to be clay.

Acid insoluble organic matter, including palynomorphs, constitutes a small part of Core 5.

Petrologic Comparison of Cores 5 and 6 with Gulf Coast Cap Rock

The mineralogy of the two cores investigated is typical of that part of the cap rock in which active alteration of anhydrite to calcite, sulfur and gypsum occurs. This region of alteration has been termed the transition zone (Taylor, 1938). This zone in Gulf Coast cap rock is characterized by sulfur, gypsum, calcite, petroleum and hydrogen sulfide, all of which were found in Cores 5 and 6. The crystal habit, structure, paragenesis, replacement relationships, and mineral associations of calcite, gypsum and sulfur in Cores 5 and 6 are similar to those described for Gulf Coast cap rock by Brown (1931), Taylor (1938), Goldman (1952), and others.

Nearly all calcite cap rock is porous, and much of it is distinctly cavernous. In fact, cavities comprise 50 per cent of some cap rock (Hanna, 1934). The rock mass represented by Core 5-1 likely had a porosity exceeding 25 per cent. In core 5-2, the pores have been largely filled with sulfur. Sulfur-bearing parts of cap rock in the Gulf coast plain average about 20 per cent (Taylor, 1938), which is approximately the proportion of sulfur in Core 5-2.

Pyrite is characteristically present in hydrogen sulfide-rich environments. The quantity, crystal size, and mode of occurrence of pyrite in Cores 5 and 6 are typical of cap rock pyrite. It has been reported in all cap rocks investigated petrologically as veins filling shear zones and as disseminations in calcite; it seldom constitutes more than one per cent of cap rock.

Chemical analyses of calcite cap rock show only a trace of magnesium, rarely as much as one per cent (Taylor, 1938); less than 0.5 per cent magnesium is present in Core 5-1.

Doubly terminated quartz crystals and quartz rosettes, such as those in Core 5, have been found throughout cap rock (Brown, 1931; Taylor, 1938; Goldman, 1952). According to Taylor, "quartz crystals are a definite characteristic of all cap rock studied," and, moreover, detrital grains of quartz, similar to those encountered in Core 5-1, occur throughout cap rock (Taylor, 1938). Quartz crystals, nearly identical to those encountered in this study, are abundant in the Louann salt (Taylor, 1937). Goldman (1952) found them in a solution residue of halite from Hockley dome, Texas and Five Islands dome, Louisiana. Quartz crystals in Core 5 are possibly syngenetic. They may be present in the halite beds inferred to exist beneath the Sigsbee Abyssal Plain.

Brown (1931) recorded the presence of a single, minute acicular tourmaline crystal in insoluble residue of cap rock anhydrite from Byran Heights dome, Texas. Whether tourmaline rhombohedrons and prisms in Core 5 actually formed within the cap rock of Challenger Knoll, or whether they formed authigenically in the inferred underlying salt and accumulated in the cap as a residue, could not be determined. Tourmaline has been reported from water insoluble residues of the German Zechstein salt (Mügge, 1913). The numerous epigenetic minerals reported from the cap rock are sulfides, carbonates or sulfates, with the possible exception of some quartz.

Formation of Challenger Knoll Cap Rock

The possible sequence of events involved in formation of the Challenger Knoll cap rock is outlined below:
(1) Diapiric salt pierced mainly clastic sediments and rose into the zone of sea water solution.
(2) An anhydrite cap subsequently formed by the accumulation and cementation of residue remaining after salt solution.
(3) Gypsum formed by the hydration of the upper part of the anhydrite cap.
(4) Petroleum migrated into pores and fractures in the gypsum and anhydrite.
(5) Anaerobic bacteria (probably *Desulfovibrio desulfuricans*), obtaining their energy and vital carbon from petroleum, extracted oxygen for their metabolism from sulfate ions and liberated hydrogen sulfide. The "free" calcium ion then indirectly combined with carbon dioxide, formed by the microbiologic oxidation of petroleum, to form calcite.
(6) The liberated hydrogen sulfide was partially oxidized to form sulfur by oxygen in the sea water penetrating the cap.

Calcite and sulfur in Cores 5 and 6 are probably indirect indices of previously consumed petroleum in the Challenger Knoll cap rock, inasmuch as petroleum is biogenically altered to hydrogen sulfide and carbon dioxide—the "raw materials" from which these rock types are formed.

Palynology

A 34.5 gram sample from Core 5-1 was processed for palynomorphs. Mineral material was removed with hydrogen chloride and hydrogen fluoride, and the organic residue was treated with Schultz's solution for one hour. Approximately 400 pollen grains and spores were recovered.

PLATE 22

A-C,G	*Classopollis* sp. 1 Mobil Research and Development Corporation, Field Research Laboratory, Slide no. 19,828 A4; X 1950; Core 5-1.
D-F,H-I	*Classopollis* sp. 2 Slide no. 19,828 A4; X 1950; Core 5-1.

PLATE 22.

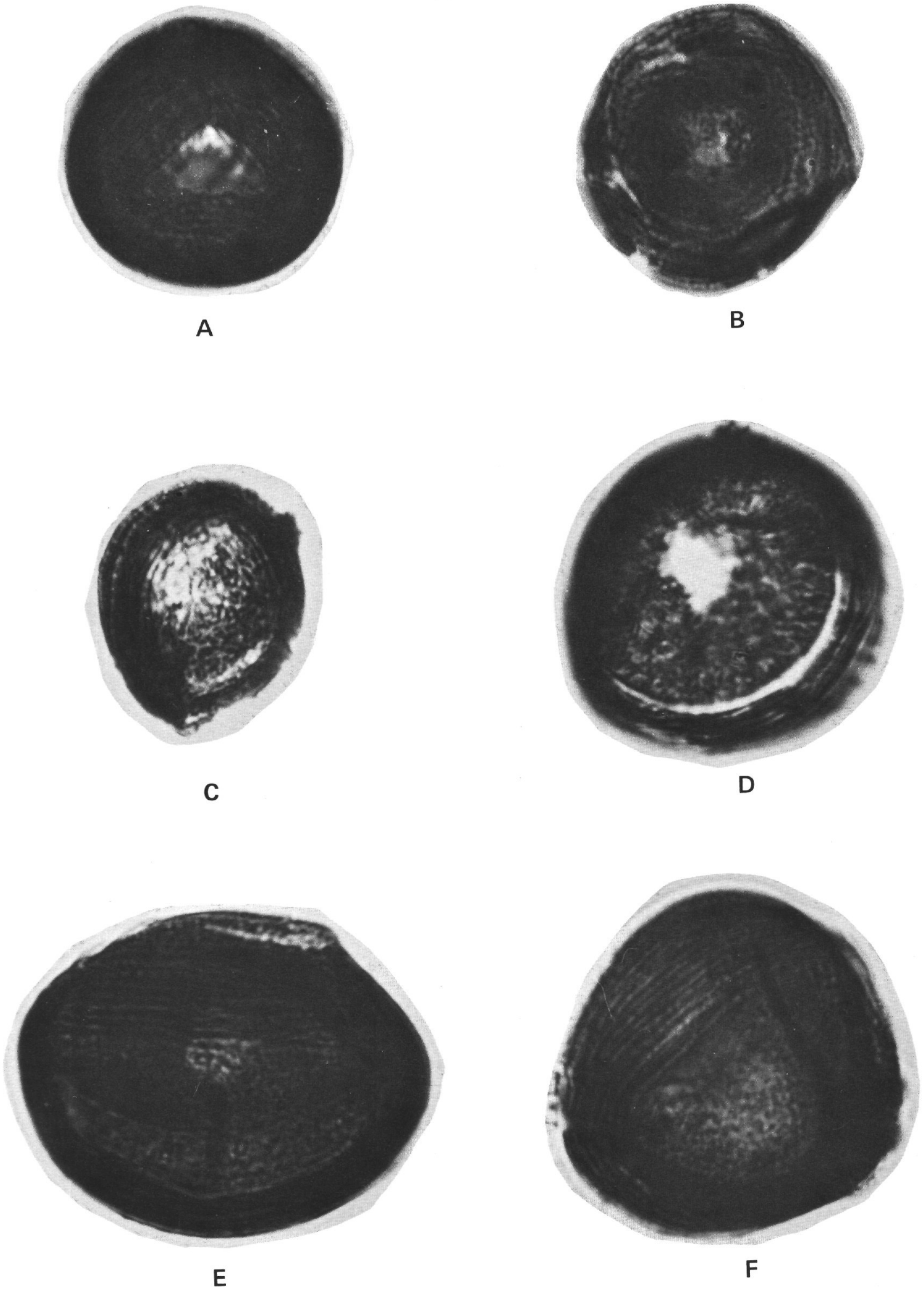
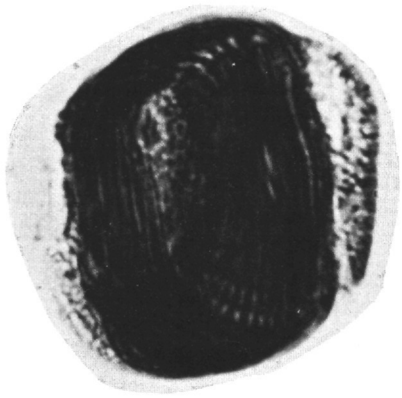
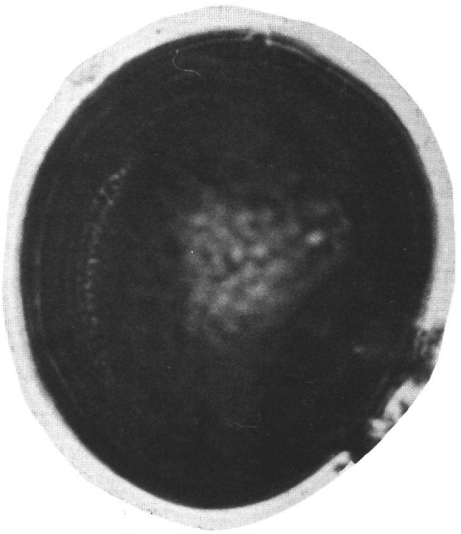


PLATE 22 - *Continued.*



G

H



I

PLATE 23

A-F	*Exesipollenites tumulus* Balme Mobil Research and Development Corporation, Field Research Laboratory, slide no. 19,828 A4; X 1950; Core 5-1.
G	cf. *Ginkgo* sp. Slide no. 19,828 A4; X 1950; Core 5-1.
H-I	Cycad-type pollen grains. Slide no. 19,828 A4; X 1950; Core 5-1.

PLATE 23.

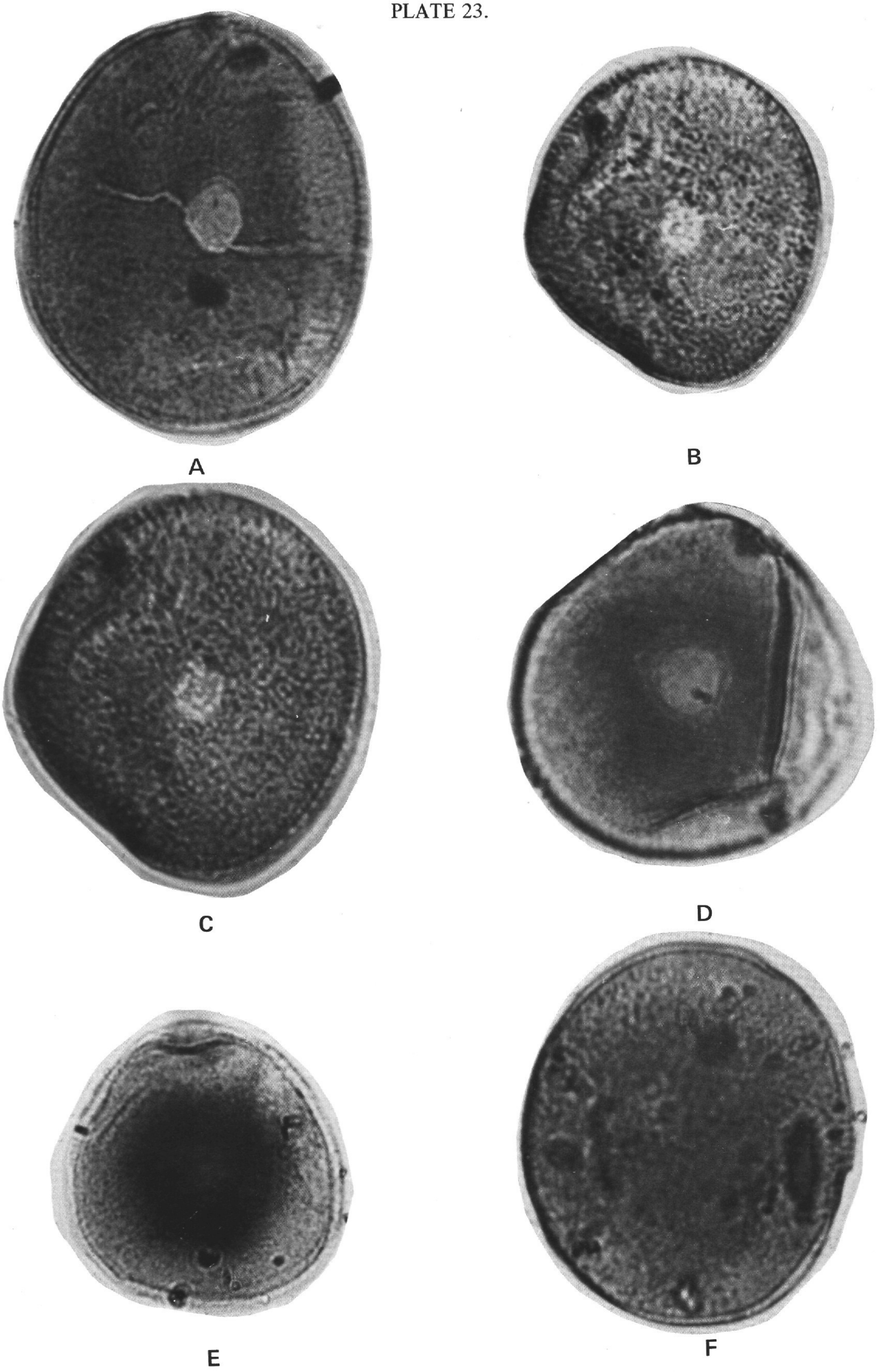
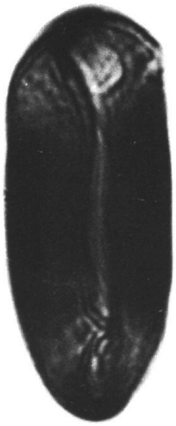


PLATE 23 - *Continued.*



G

H

I

PLATE 24

A-B Trilete spores
Mobil Research and Development Corporation, Field Research Laboratory, Slide no. 19,828 A4; X 1950; Core 5-1.

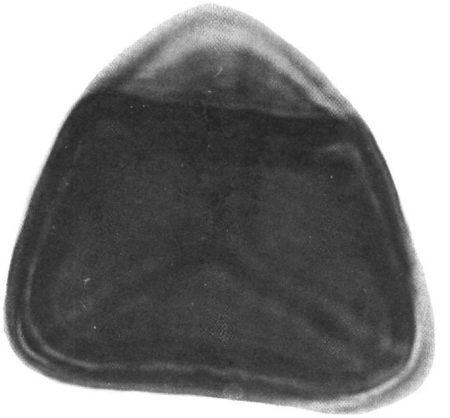
C *Applanopsis dampieri* (Balme) Goubin, Taugourdeau and Balme Slide no. 19,828 A4; X 1100; Core 5-1

D cf. *Ephedra* sp.
Slide no. 19,828 A4; X 1950; Core 5-1.

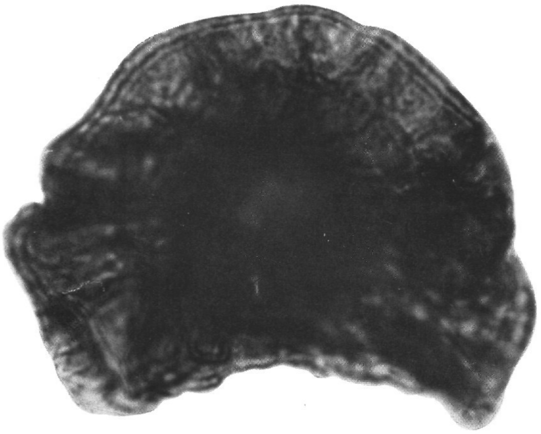
E Tracheid
Slide no. 19,828 A4; X 2300; Core 5-1.

PLATE 24.

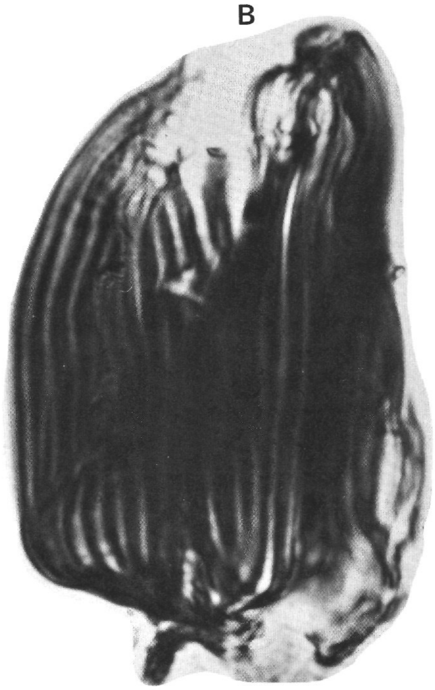
A



B

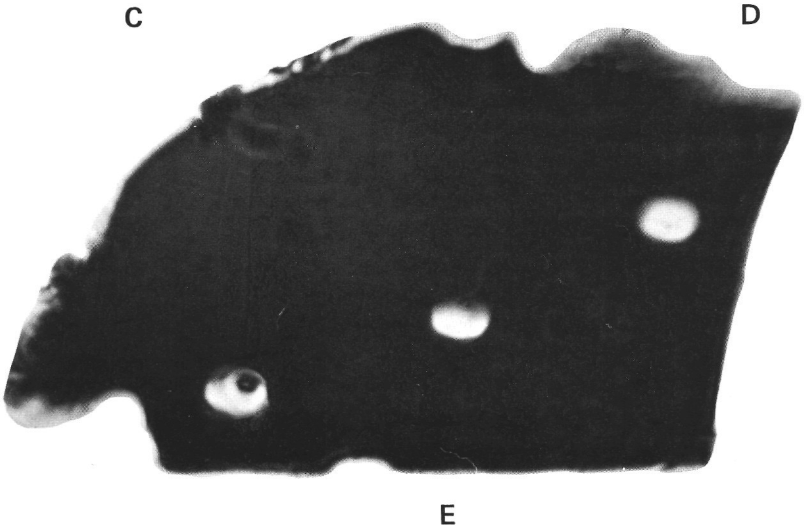


C



D

C D



E

The assemblage consists mainly of *Classopollis* spp. and *Exesipollenites tumulus* Balme, in about equal abundance. *Applanopsis dampieri* (Balme) Goubin, Taugourdeau and Balme, *Caytonia* sp., *Ginkgo* sp., *Eucommiidites* sp., *Ephedra?* sp., cycad-types and several trilete spores are also present. Many specimens are excellently preserved. These forms are illustrated in Plates 22-24.

The age of the assemblage is probably Middle or Upper Jurassic, but could be early Cretaceous. Assemblages in which *Classopollis* spp., *Exesipollenites* sp. and cycad-type pollen predominate are commonly encountered in late Jurassic strata; and, *Applanopsis dampieri* is reported to be abundant in the late Jurassic, but rare in early Cretaceous strata. *Classopollis* pollen grains generally show a marked decrease in relative abundance in early Cretaceous strata. Furthermore, striate-trilete spores, angiosperm pollen, and additional forms common in post-Jurassic strata were not encountered.

Age of the Sigsbee Salt

The palynomorph assemblage in Core 5-1 has likely been derived from diapiric salt which moved up from an underlying, thick halite bed. The fact that palynomorphs are capable of surviving halite diapirism has been demonstrated, in particular, by Baltes (1967). In their transferral from diapiric halite to calcitic cap rock, palynomorphs in Core 5-1 probably underwent a concentration of 10 to 40 times. The pollen-spore concentration in the underlying Sigsbee Salt is likely extremely low, but it is probably truly representative of the age of the salt. Recycled forms are probably absent because of the nature of the environment.

Three major pre-Tertiary salt basins surround the inferred Sigsbee Saline Basin: the United States Gulf Coast Saline Basin, the Cuban Saline Basin, and the Isthmian Saline Basin. In each case, most palynologic evidence and most stratigraphic relationships suggest that salt is of latest Triassic or Jurassic age (Imlay, 1952); Guzman *et al.*, 1953; Marquez, 1964; Murray, 1966; Contreras and Castillon, 1968; Meyerhoff and Hatten, 1968). The Sigsbee Basin Salt is most likely of Jurassic age, based on the pollen spore assemblage from Core 5-1.

Conclusions

(1) Cores 5 and 6 from Challenger Knoll have many lithologic characteristics identical with the transition zone of cap rock of salt domes surrounding the Gulf of Mexico basin.
(2) Sulfur and calcite, the major minerals in Core 5, and indirect evidence of bacterially-consumed petroleum.
(3) Diapiric halite, which has been derived from a "halite mother layer" of probably Jurassic age, underlies the Challenger Knoll cap rock.

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2.4 STUDIES PERFORMED ON SAMPLES FROM CHALLENGER KNOLL (1.3.2)

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Bartlesville, Oklahoma

Samples Received

The data reported here are for the samples, characterized and analyzed, which are listed in Table 3 with information concerning their source and date received. The two pyrite samples are from Core 4 above a possible Pliocene-Miocene unconformity. The purpose in including the data for these samples is to explore the possibility that the sulfur in these samples may have been derived from upward migration of hydrogen sulfide from the cap rock.

Data and Conclusions

Petrographic examination shows that pyrite Sample 1 from Core 4 consists of hollow rod-like particles, which have a metallic lustre and are coated with a reddish material. The particles consist of iron pyrite with a coating of gypsum. A scanning electron micrograph of the pyrite surface is shown in Plate 25A. At 5000 magnification the pyrite is a fused mass of crystals exhibiting parallel striations similar to those characteristic of pyrite crystals on a macro scale. Pyrite Sample 2, from the same core also consists of iron pyrite but without the prominent coating. Scanning electron micrographs, Plate 25B and Plate 25C show a well ordered authigenic growth of very small crystals.

The sample from Core 5-2 was shown to be essentially pure gypsum by X-ray diffraction. The scanning electron micrograph, Plate 25D shows the crystals to be small but well formed, suggesting a uniform environment for growth.

The sulfur isotopic compositions of the pyrites from Core 4, the sulfate (gypsum) from Core 6, the hydrogen sulfide from Gas Sample 1 (see Section 2.6), elemental sulfur from Core 5-2, and the organic sulfur in the oil extracted from Core 5-1, are shown in the upper half of Table 4. The normal ranges encountered in nature are provided in the last column to the right. Values are relative to NBS reference Sample Number 120. In the lower half of the table reactions are shown which are believed to take place in a cap rock and which may have led to the formation of these sulfur entities.

The two pyrite samples differ in isotopic composition by more than twelve δ units suggesting different conditions of formation. This finding is consistent with the difference in crystalline characteristics. The extremely low δS^{34} value, i.e. high concentration of S^{32}, would not likely result from reaction of hydrogen sulfide of the isotopic composition found in the gas. Two factors, however, could have lead to a hydrogen sulfide richer in S^{32} diffusing into the zone of Core 4: (1) If hydrogen sulfide is being generated from the gypsum in the vicinity of Core 6 and being lost by diffusion, the hydrogen sulfide would be expected to become progressively heavier as the S^{32} isotope in the gypsum is depleted; hence, the hydrogen sulfide which may have lead to the formation of the pyrite would have been isotopically lighter than that in the present gas. (2) In the course of diffusion through fine grained rocks, the hydrogen sulfide first reaching the zone of Core 4 would be enriched in the lighter isotope.

The isotopic value of the sulfate sulfur, or gypsum, at +30.2 is heavy, i.e. depleted in S^{32} by perhaps 10 to 15 δ units relative to that of sea water sulfate during the interval from the present through the Jurassic (Holser and Kaplan, 1966). This depletion of the S^{32} suggests that extensive biogenetic reduction of sulfate at the expense of the petroleum and associated organic matter has taken place. As shown in Table 4, this reaction should lead to a hydrogen sulfide enriched in S^{32}, i.e. with a lower δ value. As shown in the upper portion of the table, actually a decrease of about 15 δ units is observed.

Elemental sulfur is believed to be formed by oxidation of hydrogen sulfide, no mechanism for direct reduction of sulfate to sulfur having been demonstrated in nature. From the lower portion of Table 4, the oxidation of hydrogen sulfide has not been observed to involve appreciable isotopic fractionation, and any fractionation which did take place would be erased by equilibration via the polysulfide reaction. As shown in the upper part of the table, the values for the elemental sulfur in Core 5 and the hydrogen sulfide are close, differing by only one δ unit.

Petroleums rich in organic sulfur probably derive most of the sulfur through the reaction of hydrocarbons with elemental sulfur (as shown in the last reaction in Table 4). This step probably involves isotopic fractionation with the S^{32} reacting more rapidly than S^{34}. The tendency of newly generated hydrogen sulfide and unreacted sulfur to equilibrate via the polysulfide reaction would tend to prevent large differences. Data by Thode *et al.* (1958) indicate that the isotopic difference is in fact small. The relatively light value observed for the organic sulfur, therefore, is reasonable; and, in addition it may represent the reaction of isotopically lighter sulfur formed at greater depth where the gypsum is less depleted in the S^{32} isotope.

In conclusion, the mineralogical and sulfur isotopic data on samples examined are consistent with the concept that the Challenger Knoll is a salt dome structure with: (1) a cap rock consisting of calcite, partially derived from carbonate formed by oxidation of organic matter, (2) an underlayer of gypsum which has been partially depleted by biogenetic reduction to hydrogen sulfide and sulfur at the expense of petroleum and associated organic matter, (3) elemental sulfur partially deposited in the calcite cap rock and partially dissolved in and reacted with the oil, and (4) a sweeter and higher gravity petroleum at greater depth.

Methods

Mineralogy

The scanning electron micrographs were taken using the Stereoscan (Cambridge Instrument Co.). Preliminary to the photographing, the specimens were vacuum coated with gold-palladium alloy.

Mineralogy was determined by powder X-ray diffraction using the Debye-Scherer method.

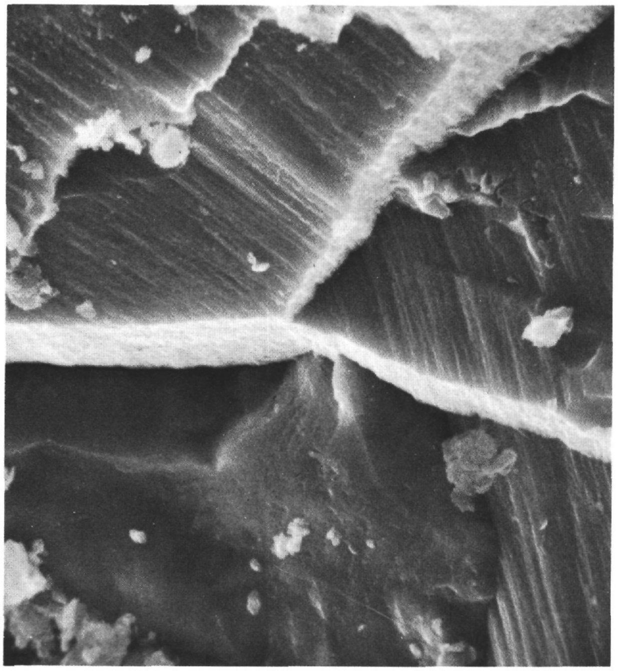

Plate 25A. *Pyrite - Sample 1.*

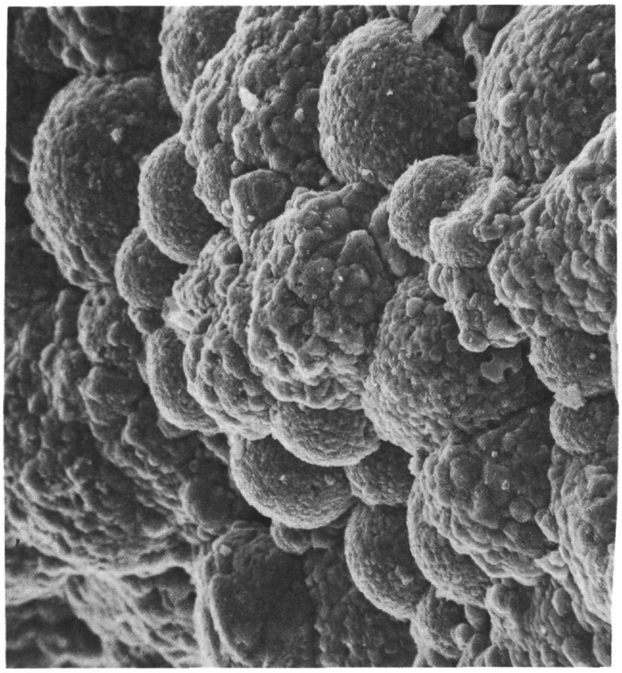

Plate 25B. *Pyrite - Sample 2.*

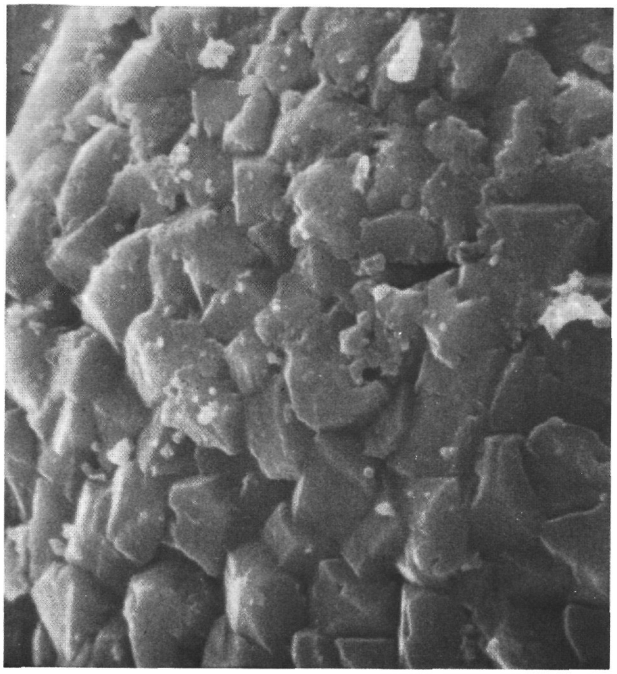

Plate 25C. *Pyrite - Sample 2.*

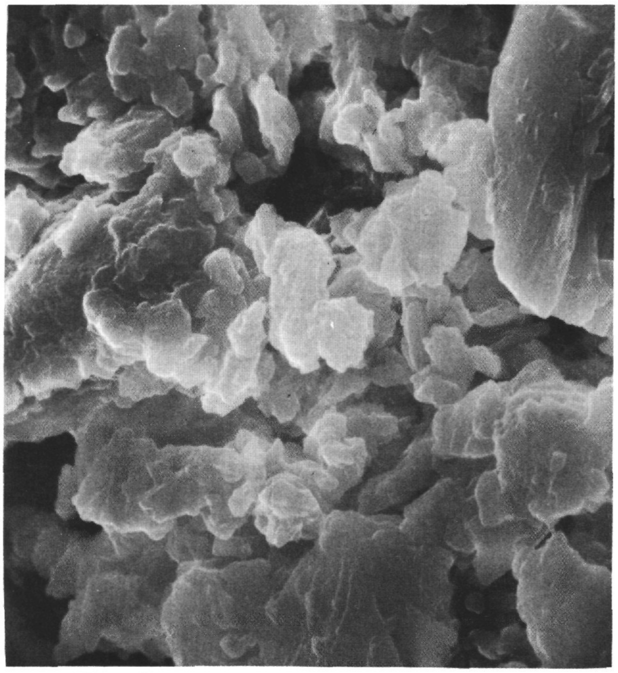

Plate 25D. *Gypsum.*

TABLE 3
Samples from Leg 1, Site 2

Type of Sample	Core No.	Submitter & Date Received
"Pyrite", Sec. 1 56.28 mg	4	J. M. Hunt - 10/25/68
"Pyrite", Sec. 2 26.20 mg	4	J. M. Hunt - 10/25/68
Core ~15 g	6	E. Bray - 10/24/68
Gas, Sample 1 (collected aboard ship)	5	J. M. Hunt - 10/11/68
Core - Sec. 2 Below oil-saturated zone ~5 g	5	E. Bray - 10/24/68
Sulfur in the oil as $BaSO_4$ - 74.5 mg	5	E. Bray - 12/2/68

TABLE 4
Sulfur Isotopic Composition of Samples from Leg 1, Site 2

Component	Sample	δS^{34}_{NBS}	Range in Nature
Pyrite	Core 4, #1	-42.9	-45 to +42
Pyrite	Core 4, #2	-30.5	
Sulfate, gypsum	Core 6	+30.2	+8 to +34
Hydrogen sulfide	Gas Sample 1	+15.2	-27 to +17
Sulfur, elemental	Core 5-2	+14.2	-16 to +22
Sulfur, organic (in oil)	Core 5-1	-6.9	-5 to +28

Reactions In a Typical Cap Rock

$$SO_4^{=} \quad + \quad H.C. \longrightarrow H_2S$$

isotopically lighter,
i.e., lower δS^{34}

$$H_2S \quad + \quad [O] \longrightarrow S^{\circ}$$

very little isotopic fractionation

$$H_2S \quad + \quad S^{\circ} \rightleftharpoons H_2S_X$$

isotopic equilibration

$$S^{\circ} \quad + \quad H.C. \longrightarrow H_2S \quad + \quad S_{organic}$$

Sulfur Isotope Analysis

Sample Separations:

Pyrite

The sample was combusted to sulfur dioxide using copper oxide as an oxidant. The sulfur dioxide was purified from other contaminants by differential freezing at -89°C (I.R. Kaplan, Personal Communication, 1967).

Gypsum

A small portion of Core 6 was dissolved in boiling water slightly acidified with hydrogen chloride. The solution was filtered and barium sulfate[4] was precipitated by addition of 0.1 N barium hydroxide. The filtered and dried sulfate was reduced by heating with excess graphite. Sulfide was washed through a porous glass filter into 1 N silver nitrate solution. The silver sulfide precipitate was collected on a 5 micron Selas silver filter.

Hydrogen Sulfide

A portion of the gas was bubbled through 1 N silver nitrate solution and filtered on to a 5 micron Selas silver filter.

Elemental Sulfur

Small pieces of elemental sulfur were hand picked from Core 5-2, and ground in an agate mortar. An excess of the sulfur was mixed with powdered silver and heated under a blanket of purified nitrogen. When reaction was complete, the temperature was raised to volatize the excess sulfur.

Organic Sulfur

The sulfur contained in the oil was received as barium sulfate. The barium sulfate was reduced to sulfide, precipitated as silver sulfide, and collected on a 5 micron Selas silver filter.

Mass Spectrometry

The mass spectrometer used for sulfur isotope analyses is a Nier-type, 35-centimeter radius, 90-degree sector, isotope ratio instrument having 12 degrees of Z-axis focusing, with a dual sample inlet system, and dual vibrating-reed electrometer detectors similar to that described by McKinney *et al.* (1950). The dual inlet system and solenoid valves used in the sulfur analyses are separate from those used in carbon analyses (see Section 2.6). Gold plating of critical components, such as kovar-glass seals, reduces "memory effects". Corrections for contributions of O^{18} and O^{17} to the measured ion currents are made and the results are reported in "δ" notation relative to the NBS isotope reference Sample No. 120. Overall precision is within 0.2 δ.

Silver sulfide samples were combusted to sulfur dioxide using copper oxide as an oxidant. Sulfur dioxide is purified from other contaminants by differential freezing at -89°C.

References

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2.5 BACTERIOLOGICAL MEDIA AND METHODS

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Sampling Methods

Samples were removed from the bottom of Core 5-1 and from the bottom of Core 5-2 with sterile, brass cork borers. A large, approximately one-inch (2.5 cm) diameter, plug was removed and a second, approximately one-half inch (1.3 cm) diameter plug was taken as the aseptic sample from the first, one-inch (2.5 cm) diameter opening.

For sampling along the lengths of Core 5-1 and Core 5-2, sterile spatulas were used to remove approximate 0.2 gram samples of core material for bacterial counts.

Bacteriological Media

Sulfur-oxidizing bacteria *(Thiobacilli):* Attempts to culture sulfur-oxidizing bacteria were made using the media of Vishniac and Santer, (1957).

Medium for *Thiobacillus thioparus:*

$Na_2S_2O_3 \cdot 5H_2O$	10.0 g
KH_2PO_4	4.0
K_2HPO_4	4.0
$MgSO_4 \cdot 7H_2O$	0.8
NH_4Cl	0.4
trace metal solution	10 ml
distilled water	1000 ml

Medium for *Thiobacillus thiooxidans:*

The above medium adjusted to *p*H 3.5 to 4.0

Medium for *Thiobacillus denitrificans*
(incubated anaerobically):

$Na_2S_2O_3 \cdot 5H_2O$	5.0 g
KNO_3	2.0
KH_2PO_4	2.0

K_2HPO_4	2.0
$NaHCO_3$	1.0
$MgSO_4 \cdot 7H_2O$	0.6
NH_4Cl	0.5
$FeSO_4 \cdot 7H_2O$	0.01
distilled water	1000 ml

One-tenth gram of sample was added to 25 milliliters of each of the above media. Incubation was at 30°C for thirty days. Cultures were observed visually for turbidity and for pellicle formation, and microscopically for bacteria at intervals during the incubation period.

Sulfate-reducing bacteria *(Desulfovibrio):*

The medium used to cultivate sulfate-reducing bacteria was R-1 medium developed for this purpose at Mobil's Field Research Laboratory. It is a lactate containing medium similar to bacteriological media generally used for cultivating these bacteria.

R-1 Medium for *Desulfovibrio:*

NaCl	10.0 g
$MgSO_4 \cdot 7H_2O$	0.5
Na_2CO_3	0.1
KH_2PO_4	0.1
Ca lactate	2.0
$(NH_4)_2SO_4$	1.0
$FeSO_4 \cdot 7H_2O$	0.05
yeast extract	1.0
agar	20.0
reducing iron powder	2.0
distilled water	1000 ml

Dilutions of samples in sterile water (1:100 and 1:1000) were used as inoculum in this agar medium.

Medium for aerobic and anaerobic general microflora: R-1 agar medium without reduced iron powder was used to cultivate aerobic and anaerobic bacteria. Dilutions of samples in sterile water (1:100, 1:1000 and 1:10,000) were used as inoculum. Anaerobic cultures were incubated at 30°C in Brewer jars. Aerobic cultures were incubated at 30°C in glass desiccators containing air. Incubation was a maximum of thirty days.

Reference

Vishniac & Sauter, 1957. *Bact. Rev.* **21**,195.

2.6 COMPOSITION OF GAS SAMPLE 1 (CORE 5) BY COMPONENTS (1.5.1)

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Samples Received

The samples for which compositional and isotopic data are reported are listed in Table 5 with information concerning their source and date received.

Data and Conclusions

When Gas Sample 1 was received it was contaminated with approximately 3.5 per cent air, probably picked up during collection in the glass jar. The compositional analysis provided in Table 6 has been corrected for this air contamination. Gas Sample 2 contained a total of 76.6 per cent oxygen, nitrogen, carbon dioxide, and argon. Hydrogen sulfide was absent, probably through oxidation to elemental sulfur. Owing to the considerable dilution with air, only the normalized concentrations of the hydrocarbons are reported in Table 7 where they are compared with the similarly normalized values for Gas Sample 1. As shown in Figure 5, Gas Sample 2 is enriched in the components of higher carbon number, the degree of enrichment increasing with carbon number. The difference in composition probably is the consequence of fractionation or preferential loss of the more volatile components during evolution of the gas from the core.

In Figure 6, the carbon isotopic compositions of the first five members of the hydrocarbon series in Gas Sample 1 and the first three in Gas Sample 2 are plotted versus carbon number. The methane, ethane and propane in Gas Sample 2 is slightly depleted in regard to the lighter C^{12}, i.e. the δ value is somewhat higher or less negative than for the same components in Gas Sample 1. This shift in isotopic composition also is a consequence of the fractionation which occurred as was lost from the core.

At the extreme right of Figure 6, the carbon isotopic composition of topped oil extracted from Core 5 is shown. The value is near the midpoint of the range attributed to oils of marine origin, and slightly to the heavy side of the mode which is away from the range attributed to terrestrial origin.

At the left of Figure 6, the carbon isotopic value of the calcite sample from Core 5-1, is shown. The value is relatively light, as most marine limestones go, suggesting that part of the carbon has been derived from the reaction

$$\text{H.C.} + SO_4^{=} \longrightarrow H_2S + CO_3^{=}$$

where H.C. is petroleum or associated organic matter.

TABLE 5
Samples from Leg 1, Site 2

Type of Sample	Core Number	Submitter & Date Received
Gas, Sample 1 (collected aboard ship)	5	J. M. Hunt - 10/11/68
Gas, Sample 2 (collected in Mobil laboratory)	5	E. Bray - 10/24/68
Core 5-1 Oil-saturated zone ∿ 5 g	5	E. Bray - 10/24/68
Core 5-2 Below oil-saturated zone ~5 g	5	E. Bray - 10/24/68

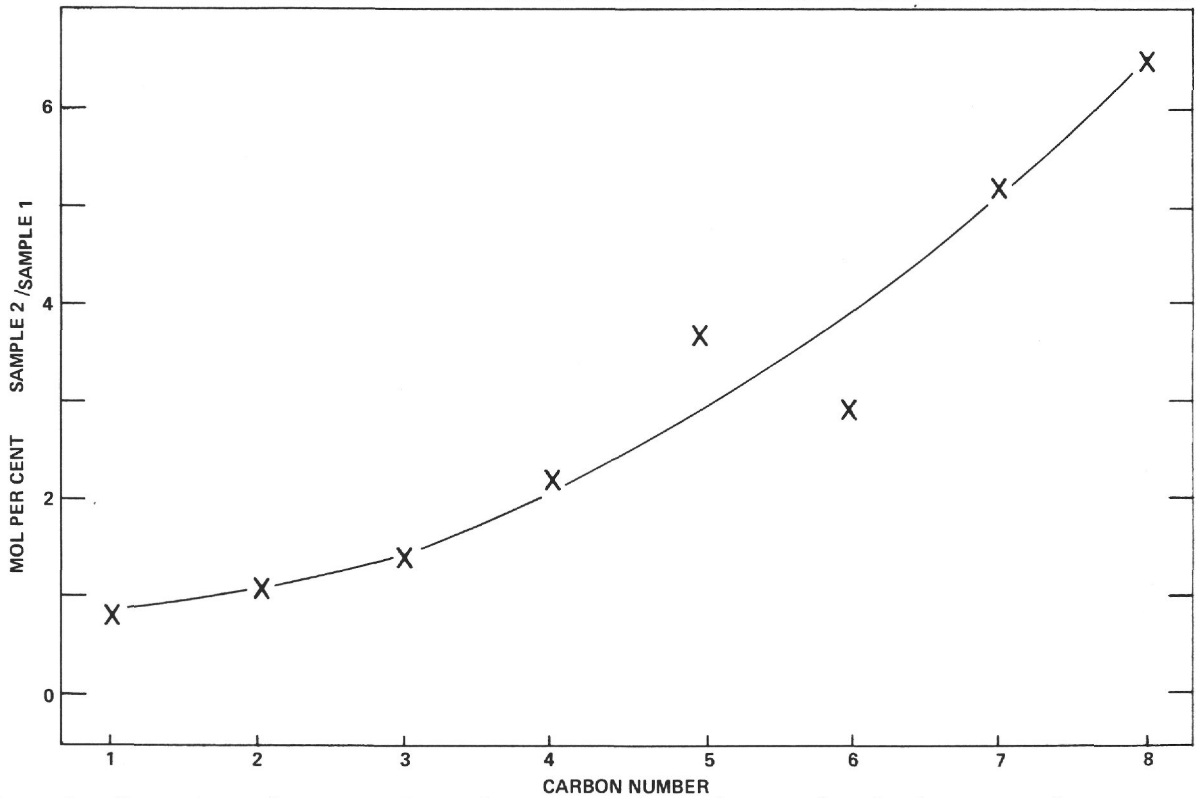

Figure 5. *Comparison of concentrations of components by carbon numbers in the gas samples.*

In Figure 7, the carbon isotopic composition of the low molecular weight components of Gas Sample 1 are compared with the values for two petroleums, the reservoirs of which are underlain by salt. In both cases the rate of increase in the δ value with carbon number is less pronounced than in the gas from Core 5. A steep rise in the δ value is interpreted as indicating that the petroleum encountered in the Challenger Knoll is geochemically young.

The component composition of the gas from Core 5 is typical of a gas associated with a crude oil of intermediate API gravity. The carbon isotopic value for the oil indicates that the source rocks were deposited in a typical marine environment. The shape of the curve representing carbon isotopic composition versus carbon number is normal for well developed but geochemically young crude oils. The shallow depth of burial allows in this case the term "geochemically young" to

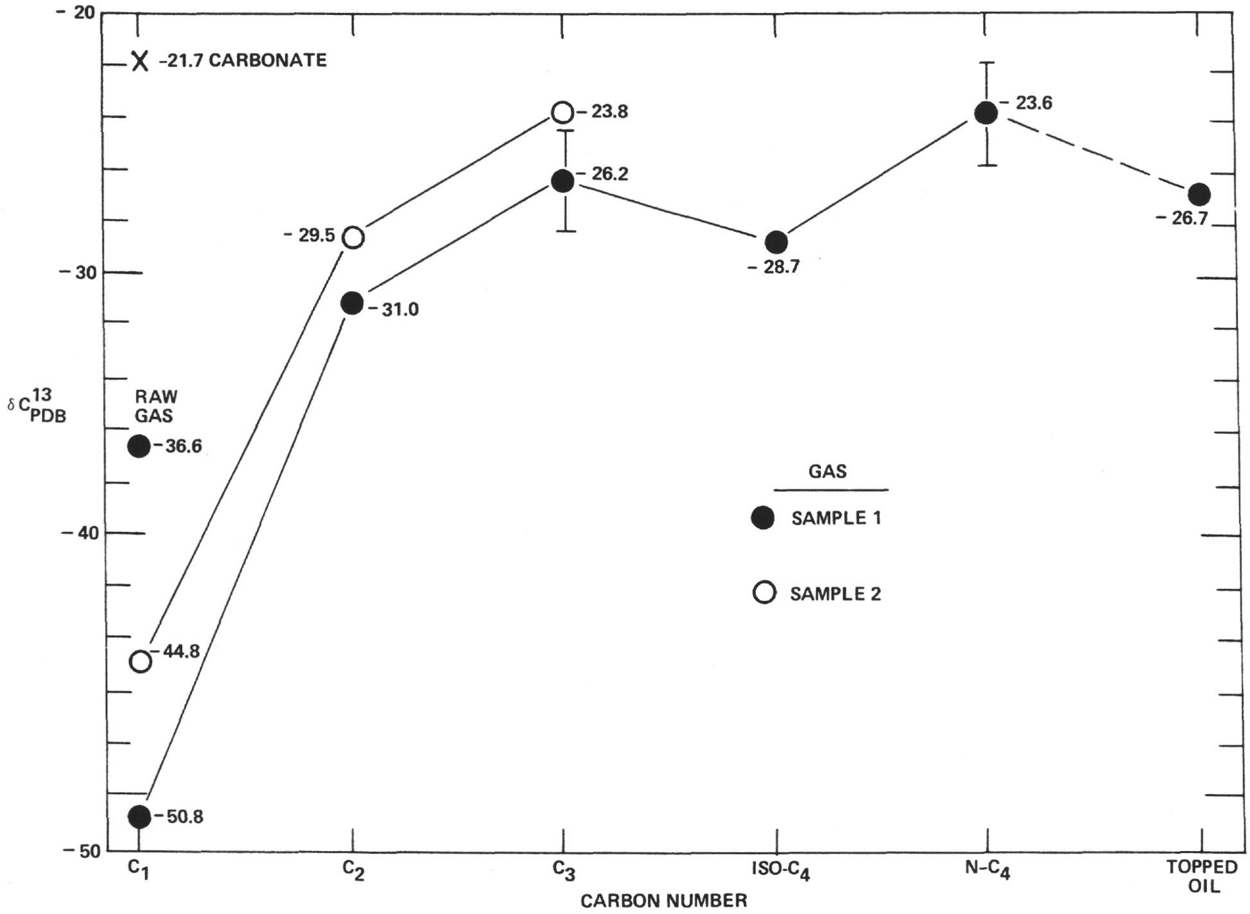

Figure 6. *Comparison of the carbon isotopic composition of the individual low molecular weight gas components of the gas samples, the topped oil, and the calcite of Core 5.*

encompass a relatively long interval of geologic time whereas the elevated temperature in proximity to a salt plug would tend to shorten the permissible geologic age. The calcite carbon value suggests considerable oxidation of the petroleum and associated organic matter with formation of hydrogen sulfide and elemental sulfur (see Section 2.4). These events also tend to shorten the permissible geologic age. Accordingly, it is believed that the oil encountered in the Challenger Knoll is relatively young geologically as well as geochemically.

Methods

Gas Component Analysis

Helium was analyzed using a CEC Model 21-103B mass spectrometer. Nitrogen, oxygen plus argon, and hydrocarbons through the pentanes were measured by gas chromatography using the NGPA Standard 2261-64 method. Components greater than pentanes were run in a Perkin-Elmer Model 900 Gas Chromatograph equipped with a flame ionization detector and a 150 foot (45.7 m) by 0.01 inch (0.03 cm) I.D. Golay column coated with squalane.

Carbon Isotope Analysis

Sample Separations:

Oil

A tarry, oil-like bitumen was recovered from approximately 5 grams of Core 5-1. The unconsolidated sample, as received, was repeatedly rinsed with methylene chloride until no further discoloration of the solvent was noted. Solvent was evaporated from the filtered solution on a rotary evaporator at ~65°C under reduced pressure of ~0.5 atmosphere until no further weight loss was observed.

Gas

Components were separated by gas chromatographic procedure developed for the purpose to assure quantitative recovery and to avoid alteration of isotopic composition. Precision in the isotopic measurement

TABLE 6
Composition of Gas Sample 1 by Component

Component	Concentration, mol %
Helium	<0.02
Hydrogen sulfide	2.94
Nitrogen	1.23
Carbon dioxide	0.77
Methane	63.1
Ethane	13.5
Propane	10.8
Isobutane	6.41
n-butane	0.49
Neo-pentane	0.033
Iso-pentane	0.107
n-pentane	0.010
Neo-hexane	0.028
2-methylpentane	0.208
3-methylpentane	0.066
n-hexane	0.0066
2,2-dimethylpentane	0.0018
2,4-dimethylpentane	0.031
Methylcyclopentane	
Benzene	0.0057
Trimethylbutane	
3,3-dimethylpentane	0.0014
Cyclohexane	0.0071
2-methylhexane	0.0044
2,3-dimethylpentane	0.017
3-methylhexane	0.011
Dimethylcyclopentane	0.026
n-heptane	0.0013
2,2-dimethylhexane	0.0014
Methylcyclohexane	0.028
Toluene	0.162
Dimethylcyclohexanes	0.0080
Other C_8 paraffins and naphthenes	0.023
n-octane	0.0001
Ethylbenzene and ethylcyclohexane	0.0017
m-and *p*-xylene	0.0012
o-xylene	0.0002
C_9 paraffins and napthenes	0.0013

TABLE 6 - *Continued*

Component	Concentration, mol %
n-nonane	0.0003
C_{10}'s	0.0033
C_{11}'s	0.0005

TABLE 7
Composition of the Hydrocarbon Fractions of the Gas

Component	Concentration, mol % Sample 1	Sample 2
Methane	66.3860	51.8919
Ethane	14.1814	15.3960
Propane	11.3451	14.2381
Isobutane	6.7388	13.2946
n-butane	0.5118	1.3295
Neo-pentane	0.0352	
Iso-pentane	0.1130	0.7719
n-pentane	0.0107	0.0858
Neo-hexane	0.0299	0.0232
Cyclopentane		0.9606
2,3-dimethylbutane		
2-methylpentane	0.2186	0.1883
3-methylpentane	0.0689	0.3675
n-hexane	0.0069	0.0279
2,2-dimethylpentane	0.0018	0.1402
Methylcyclopentane	0.0321	
2,4-dimethylpentane		0.0330
Benzene	0.0061	0.0193
Trimethylbutane		
3,3-dimethylpentane	0.0014	0.0069
Cyclohexane	0.0075	0.3053
1,1-dimethylcyclopentane		0.1235
2,3-dimethylpentane	0.0178	
2-methylhexane	0.0046	0.0244
3-methylhexane	0.0116	0.0678
Dimethylcyclopentanes	0.0269	0.1411
n-heptane	0.0013	0.0030
2,2-dimethylhexane	0.0014	

TABLE 7 - *Continued*

Component	Concentration, mol %	
	Sample 1	Sample 2
Methylcyclohexane	0.0290	0.1754
Trimethylcyclopentanes		0.0343
Toluene	0.1701	0.0270
Dimethylcyclohexanes	0.0084	0.0600
Other C_8 paraffins and napthenes	0.0246	0.1484
n-octane	0.0001	
Ethylbenzene and ethylcyclohexane	0.0018	0.0116
m-xylene		0.0081
p-xylene	0.0013	0.0004
o-xylene	0.0002	0.0013
Other C_9 paraffins and napthenes	0.0014	0.0742
n-nonane	0.0003	
Decanes	0.0035	
C_{10}'s +		0.0193
C_{11}'s +	0.0005	

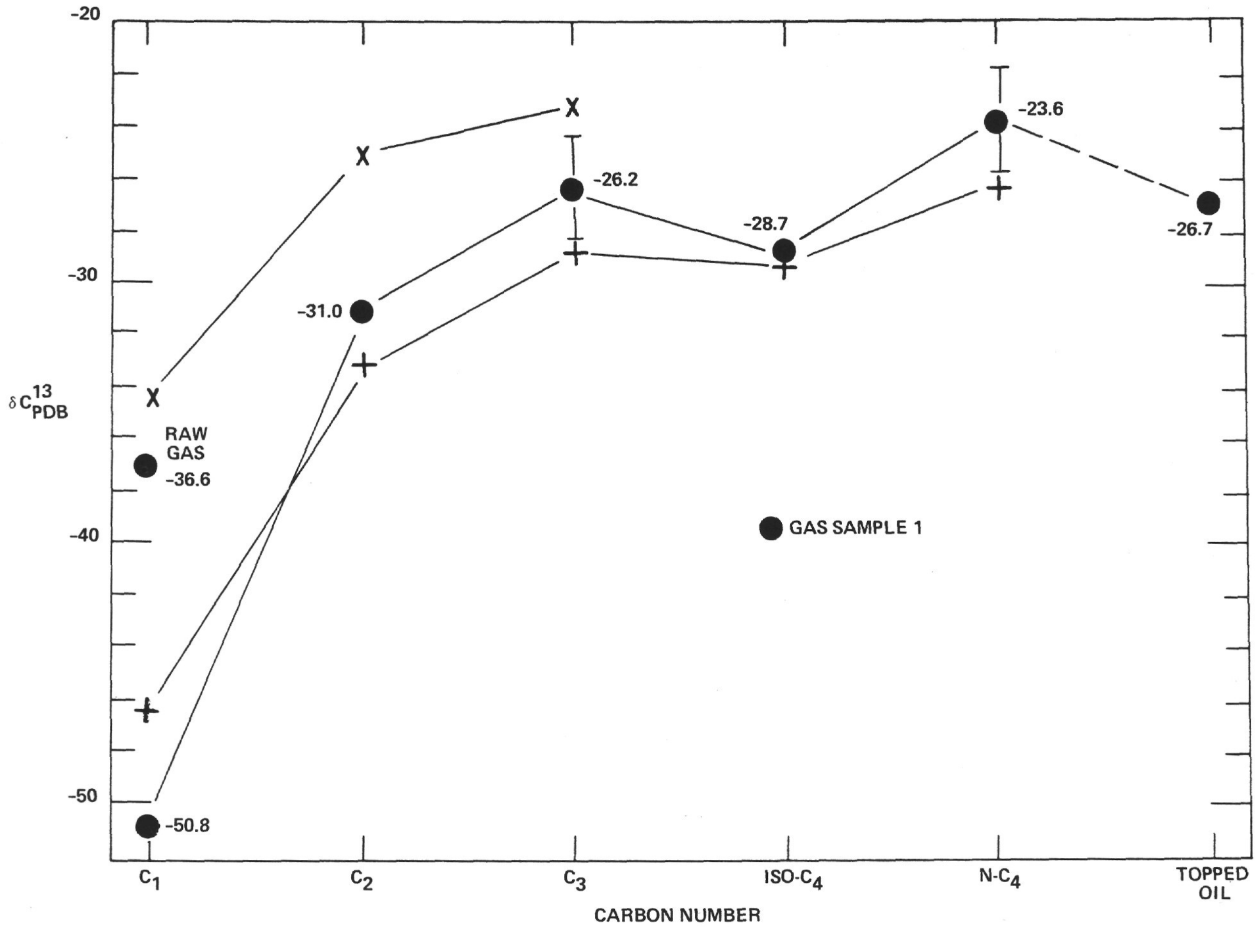

Figure 7. *Comparison of the carbon isotopic composition of the individual low molecular weight gas components of Gas Sample 1 and two petroleums underlain by salt.*

for components present in appreciable quantity is within 0.2δ.

Mass Spectrometry

The mass spectrometer used is a Nier-type 35-centimeter radius, 90-degree sector, isotope ratio instrument having 12-degrees of Z-axis detectors similar to that described by McKinney *et al.* (1950). Isotope measurements are made on the m/e = 45 and m/e = 44 ions using carbon dioxide as the working gas. Corrections to the m/e = 45 ion current for $C^{12}O^{17}O^{16}$ contribution are made as described by Craig (1957). Isotopic compositions are reported using the "δ-" notation relative to the PDB standard (Craig 1953, 1957). Instrument precision is ± 0.05δ.

Organic carbon samples were combusted to carbon dioxide for mass spectrometry in a vacuum system modified from Craig (1953). Oxidation was carried out at 925°C over a copper oxide catalyst within an oxygen atmosphere of 4-centimeter Mercury pressure. Sulfur oxides were removed by a hot manganese dioxide catalyst (Sackett, W. M., Personal Communication, 1965). Carbon dioxide was purified of water by differential freezing at -123°C.

References

Craig, H., 1953. *Geochim. et Cosmochim. Acta.* **3** 53.

Craig, H., 1957. *Geochim. et Cosmochim. Acta.* **12** 133.

McKinney, C. R., McCrea, J. M., Epstein, S., Allen, H. A., and Urey, H. C., 1950. *Rev. Sci. Instrum.* **21**, 724.

2.7 ANALYSIS OF ORGANIC MATTER IN CORE 5, LEG 1, SITE 2 (1.5.2)

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The following report described the results of a series of geochemical analyses performed on the organic matter in Core 5, Leg 1, Site 2 of the Deep Sea Drilling Project. These analyses were performed to determine to what extent the material in the core resembles natural crude oils.

Two samples were received from the Mobil Research and Development Corporation Laboratory in Dallas: 1) The rock sample was assigned our sample code number GM-S-101. This sample was made up of a poorly consolidated mass containing lumps of rock of various sizes. It was analyzed as received; whenever possible, the portion used in an analysis was described as consolidated or unconsolidated depending on its general appearance. 2) A benzene solution of organic material was assigned our sample code number GM-0-101. This solution had been prepared by Mobil personnel by water-washing the benzene-methanol solution resulting from the extraction of a large piece of core. Preliminary to the analyses, 400 milliliters of the benzene solution was concentrated in a 1 meter long 5.8 millimeter ID, vacuum jacketed Vigreux still. This concentration step produced 7 milliliters of a benzene solution containing approximately 65 weight per cent extracted material.

Analytical Procedures and Results

Preparation of GM-0-101 for Sulfur, Asphaltene and Hydrocarbon Type Determination

Approximately 1 milliliter of the concentrated solution of GM-0-101 was placed in a small flask and brought to constant weight on a sand bath at 60° C. Experience has shown that the materials boiling above 325°C are quantitatively retained in this procedure.

Determination of Sulfur

The method used was ASTM method D-1552-58T. An induction type furnace was used for the combustion of the sample in a stream of oxygen. The produced sulfur dioxide was determined by iodate titration with starch as an indicator.

Sulfur content of the high boiling portion of the extract which had been brought to constant weight at 60°C was determined to be 4.94 per cent as shown in Table 8.

Determination of Asphaltenes

Twenty milliliters of 2,3 dimethyl-butane were added to 1.040 grams of the high-boiling portion of the extract brought to constant weight at 60°C. The insoluble fraction (asphaltenes) was collected on a fine-porosity filter and weighed after it had been allowed to dry for 4 hours at 105°C. This fraction represents 14.0 per cent of the high boiling portion of the extract.

TABLE 8
Sulfur, Asphaltene and Hydrocarbon Type Analyses for the Heavy Fraction of GM-0-101

Sulfur, % wt		4.90
		4.97
Asphaltenes, % wt		14
Fraction soluble in 2,3 dimethyl-butane, % wt		86
Saturated hydrocarbons	30	
Aromatic hydrocarbons	37	
Hetero Compounds	19	

The asphaltene-free diisopropyl-soluble material was recovered by evaporation of the solvent under reduced pressure at 70°C. This fraction represents 86.0 per cent of the total sample. The result of the asphaltene determination is shown in Table 8.

Hydrocarbon-Type Determination

Hydrocarbon-type analysis was made on the asphaltene-free fraction described in the preceding section.

Type separation was done on a 15 milliliter chromatographic column (250 mm long and 10 mm ID) packed with 10 milliliters of Davison grade 922 silica gel and 5 milliliters of Harshaw grade A1-0102P alumina. The sample was placed on the column as a solution in a mixture of one part cyclopentane and two parts *n*-pentane. Three successive fractions were eluted. Fraction one, consisting of saturated hydrocarbons, was eluted with 27 milliliters of *n*-pentane. The second fraction, containing the aromatic hydrocarbons and some sulfur containing cyclic compounds, was eluted with 50 milliliters of a 60/40 mixture of *n*-pentane and benzene. Fraction three, being composed of polar hetero compounds, was eluted with 70 milliliters of an 80/20 mixture of benzene and isoprophyl alcohol. The material remaining on the column was made up primarily of high molecular weight hetero-compounds.

Results of the separations are summarized in Table 8.

Volatility Distribution of the Oil in the Core and in the Benzene Extract

A gas liquid chromatographic method was used to determine the volatility distribution of the pore fluid in the solid sample, GM-S-101, and also of the concentrated

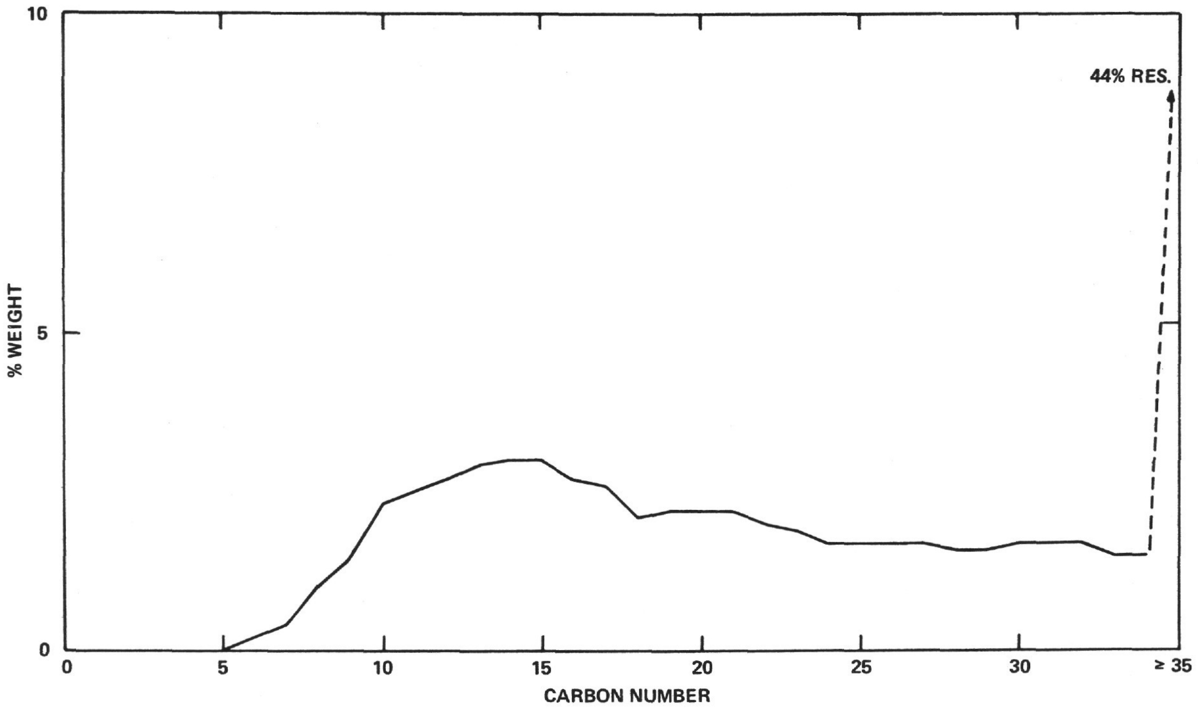

Figure 8. *Volatility distribution - Core 5, Leg 1 - combined results of GM-S-101 and GM-O-101.*

benzene extract, GM-0-101. To get the overall distribution the two analyses were combined on the basis of the C_{16} through C_{25} overlap. This was necessary since it was felt that the high boiling material could not be determined accurately on the rock sample and since the low boiling components of the extracted oil were lost during extraction and evaporation procedures.

The column used in the analysis was a 4 foot long (1.23 m) by 0.25 inch (0.63 cm) O.D. tubing packed with 10 per cent OV-1 silicone gum on 80/100 mesh chromosorb W. The temperature was programmed from 2° to 350°C during the analysis.

Residue boiling above C_{34} was determined by use of a method based on the sensitivity of the instrument to a milligram of a low viscosity lube oil that boils in the C_{13} to C_{34} range. The residue value thus obtained was accurate to 10 per cent or better.

Results of this analysis are shown in Table 9 and Figure 8.

Carbon Number Distribution of the High Molecular Weight *n*-Paraffins Isolated from the Extract GM-0-101

The saturated hydrocarbon fraction (prepared as described above) was further separated by urea adduction followed by 5A molecular sieve treatment into an isoparaffin plus cycloparaffin concentrate and a *n*-paraffin concentrate. The *n*-paraffin concentrate represented 0.4 to 1.0 weight per cent of the high-boiling portion of the extract brought to constant weight at 60°C. It was analyzed by gas-liquid chromatography for carbon number distribution. A 100 foot (30.48 m), 0.02 inch (0.05 cm) I.D. stainless steel column, coated with SE-30 silicone gum, was used under programmed temperature conditions. The carbon number distribution of the concentrate is shown in Table 10.

Boiling Point and Type Distribution of the Heavy Hydrocarbons Isolated from the Extract GM-0-101

The isoparaffin plus cycloparaffin fraction isolated by adduction and the aromatic fraction prepared as described above were distilled in a microstill (Blumer, 1962). The boiling point distribution is shown in Figure 9.

Analysis of C_{10} to C_{20} *n*-Paraffins and Isoprenoid-Isoparaffins in Sample GM-S-101

A 37.6 gram sample of the loosely consolidated Core Sample GM-S-101 was extracted with *n*-pentane for 24 hours in a small Soxhlet extractor. The condenser water was cooled to about 39°F. An internal standard of a one to one ratio mixture of trans- and cis-decalin was added to the extracting solvent in order that the concentrations of individual hydrocarbons could be calculated. Although the decalins were not completely resolved from the background in the chromatogram, they were added in quantities large enough (2.00 mg) to minimize the influence of the hydrocarbon background.

TABLE 9
Volatility Distribution, Weight Per Cent

Carbon Number	B.P., °C at 760 mm	Core 5, Leg 1 Combined Sample
5	36.1	0.0
6	68.7	0.2
7	98.4	0.4
8	125.7	1.0
9	150.8	1.5
10	174.1	2.3
11	195.9	2.5
12	216.3	2.7
13	235.4	2.9
14	253.6	3.0
15	270.6	3.0
16	286.8	2.7
17	301.8	2.6
18	316.1	2.1
19	329.7	2.2
20	342.7	2.2
21	355.6	2.2
22	367.6	2.0
23	379.0	1.9
24	389.9	1.7
25	400.4	1.7
26	410.5	1.7
27	420.2	1.7
28	429.6	1.6
29	438.6	1.6
30	447.3	1.7
31	456.0	1.7
32	464.0	1.7
33	472.0	1.5
34	479.0	1.5
>34	>479.0	44.0

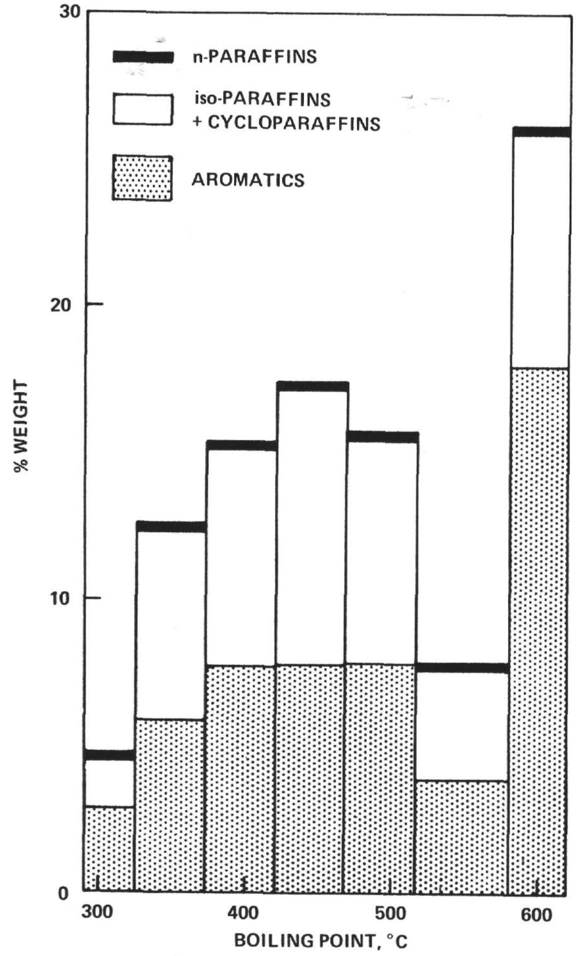

Figure 9. *Boiling point and hydrocarbon-type distribution of the heavy hydrocarbons isolated from the Extract GM-0-101.*

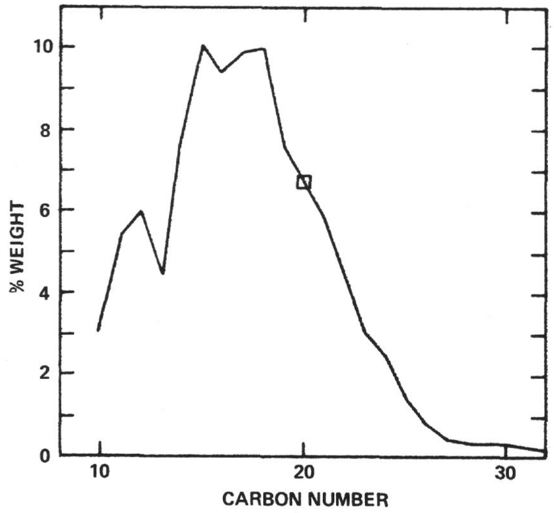

Figure 10. *C_{10}-C_{32}-n-Paraffins Distribution. Core 5, Leg 1.*

After a 24-hour extraction period the hydrocarbon solution of about 50 milliliters was concentrated to about 2.5 milliliters in a 3-foot (0.91 m), long 0.5 inch (1.27 cm) I.D. Vigreux still. The concentrate was then chromatographed to remove the aromatics. This was done on a 15 milliliter column packed with Davison 912 silica gel. Twenty-five milliliters of isopentane were used for elution. Saturated hydrocarbons and solvent were collected and again distilled in the small Vigreux still to a volume of about 2 milliliters. The concentrate was then analyzed by gas liquid chromatography. A 400 foot (121.76 m), 0.02 inch (0.05 cm) I.D., stainless steel column was used. It was coated with 10 per cent SF-96 silicone oil plus 0.5 per cent Igepal CO-880 surfactant in a 50/50 volume per cent solution of acetone and ether.

The distribution of the C_{10} to C_{20} *n*-paraffins in the GM-S-101 rock is shown in Column II of Table 10, along with that of the higher boiling *n*-paraffins isolated from the extract GM-0-101. Both sets of results were combined on the basis of the *n*-eicosane (C20) concentration. The combined and normalized distribution of the C_{10} to C_{34} *n*-paraffins is shown in Column III Table 10 and in Figure 10.

The distribution of isoprenoid isoparaffins and the *n*-paraffins is shown in Table 11.

Mass Spectrometric Analysis of the Isoparaffin + Cycloparaffin Fractions Boiling in the Ranges 325°C to 370°C, 370°C to 420°C, and 420°C to 470°C

Three isoparaffin + cycloparaffin fractions boiling within the range 325°C to 470°C (prepared as described above) were analyzed by mass spectrometry.

The instrument used was a CEC Model 21-103-C mass spectrometer, modified to analyze high boiling petroleum fractions. It was operated at a cracking pattern of 12.5 calculated from the ratio of the m/e 85 to 225 peaks of *n*-hexadecane. The method used was that developed by Hood and O'Neal (1959).

The results are shown in Table 12.

Analysis of C_4 Through C_7 Hydrocarbons in Sample GM-S-101

A sample weighing between 0.5 and 5 grams was introduced along with a brass ball into a small brass grinding cylinder and ground on a shaking machine. The ends of the cylinder were equipped with quick-connect fittings that were normally closed. After one minute of grinding, the cylinder was placed in an oven at 120°C and connected to a supply of pure helium on one end and to a sample drying and trapping system on the other end. Helium was allowed to pass through the sample for one and one-half hours. The effluent flowed through a U-tube filled with magnesium perchlorate to remove the water. The magnesium perchlorate was held at 60°C and did not adsorb the hydrocarbons. Hydrocarbons which emerged from the water trap were condensed in another U-tube filled with silica gel and glass beads and held at liquid nitrogen temperature. At

TABLE 10
***n*-Paraffin Carbon Number Distribution, % Wt**

Carbon Number	B.P., °C at 760 mm	I Sieve Separated Fraction From GM-0-101	II GM-S-101	III I & II Combined
10	174.1	-	4.2	3.3
11	195.9	-	6.7	5.4
12	216.3	-	7.4	6.0
13	235.4	-	5.4	4.4
14	253.6	-	9.8	7.9
15	270.6	0.1	12.5	10.1
16	286.8	2.0	11.6	9.4
17	301.8	7.8	12.2	9.9
18	316.1	13.4	12.4	10.0
19	329.7	15.7	9.4	7.6
20	342.7	15.8	8.3	6.7
21	355.6	13.5	-	5.8
22	367.6	10.1	-	4.3
23	379.0	7.0	-	3.0
24	389.9	5.9	-	2.5
25	400.4	3.4	-	1.4
26	410.5	1.9	-	0.8
27	420.2	0.9	-	0.4
28	429.6	0.6	-	0.3
29	438.6	0.6	-	0.3
30	447.3	0.6	-	0.3
31	456.0	0.4	-	0.2
32	464.0	0.2	-	0.1
33	472.0	0.1	-	0.0
34	479.0	0.0	-	0.0

TABLE 11
Analysis of Isoprenoid Isoparaffins and Normal Paraffins in Sample GM-S-101 by Gas Chromatography

Isoprenoid Isoparaffins ppm		Normal Paraffins ppm	
IPI_{13}	14.0	nC_{10}	13.0
IPI_{14}	14.2	nC_{11}	20.8
IPI_{15}	17.6	nC_{12}	23.1
IPI_{16}	21.9	nC_{13}	16.9
IPI_{18}	21.4	nC_{14}	30.4
IPI_{19}	15.9	nC_{15}	38.9
IPI_{20}	21.4	nC_{16}	36.1
		nC_{17}	38.0
		nC_{18}	38.4
		nC_{19}	29.3
		nC_{20}	25.9

TABLE 12
Mass Specrometric Analysis of the Isoparaffin + Cycloparaffin Fractions Boiling in the 325°C to 470°C Range Isolated From Sample GM-0-101

Molecular Constituents Volume Per Cent	Sample Designation		
	325-370°C	370-420°C	420-470°C
Paraffins[a]	34	29	22
Cycloparaffins by Number of Rings per Nucleus			
1	22	22	21
2	19	19	20
3	12	12	15
4	10	11	14
5	3	5	4
6	-	2	1
Monoaromatics	0	0	3

[a] Calculated on the assumption that all paraffins are isoparaffins.

TABLE 13
Analysis of Hydrocarbons Boiling Through 114°C For Sample GM-S-101 and Two Low-Gravity Gulf Coast Tertiary Oils

	GM-S-101				Gulf Coast Tertiary Oils	
Date	10/28/68	10/28/68	11/1/68	11/27/68	Spindle Top Field	Stratton Ridge Field
Sample Wt (g)	1.228	1.029	4.9	5.0		
Appearance of Sample	Consolidated Rock	Unconsolidated Rock	Unconsolidated Rock	Consolidated Rock	Cap Rock Oil	Oil
Components						
Butane	0.28	0.31	0.52	0.14	1.46	15.10
2-Methylpropane	0.63	1.39	0.91	1.92	3.85	11.48
n-Pentane	1.18	1.55	0.96	2.69	1.00	7.76
2-Methylbutane	0.71	0.57	1.17	2.30	8.21	9.84
2,2-Dimethylpropane	0.03	0.15	0.13	0.08	0.00	0.00
Cyclopentane	1.18	0.99	1.14	0.73	0.37	1.54
n-Hexane	0.22	0.34	0.81	0.31	0.97	3.29
2-Methylpentane	0.51	0.49	0.97	0.73	2.93	4.06
3-Methylpentane	2.00	1.97	2.77	2.50	4.67	3.24
2,2-Dimethylbutane	0.06	0.04	0.17	0.06	4.67	3.30
2,3-Dimethylbutane	0.47	0.38	0.66	0.63	7.51	4.25
Methylcyclopentane	2.06	2.47	2.77	1.79	1.14	4.81
Cyclohexane	12.26	14.33	14.33	11.15	0.97	2.42
Benzene	0.72	1.54	1.39	0.69	2.58	2.29
n-Heptane	0.59	0.75	1.40	0.76	0.97	1.56
2-Methylhexane	1.33	1.60	1.76	1.07	1.93	1.37
3-Methylhexane	4.08	4.71	4.62	3.96	4.11	2.30
3-Ethylpentane	2.04	2.36	2.19	1.83	1.57	0.44
2,2-Dimethylpentane	0.26	0.30	0.39	0.17	2.83	0.95
2,3-Dimethylpentane	5.93	6.90	6.70	6.23	6.57	1.98
2,4-Dimethylpentane	0.74	0.88	1.06	0.62	3.23	1.46
3,3-Dimethylpentane	0.42	0.50	0.54	0.28	2.26	0.95
2,2,3-Trimethylbutane	0.00	0.04	0.06	0.06	0.00	0.00

TABLE 13 - *Continued*

	GM-S-101				Gulf Coast Tertiary Oils	
Date	10/28/68	10/28/68	11/1/68	11/27/68	Spindle Top Field Cap Rock Oil	Stratton Ridge Field Oil
Sample Wt (g)	1.228	1.029	4.9	5.0		
Appearance of Sample	Consolidated Rock	Unconsolidated Rock	Unconsolidated Rock	Consolidated Rock		
Methylcyclohexane	22.91	20.82	18.48	24.00	0.82	3.65
Ethylcyclopentane	2.46	2.23	1.82	2.36	0.67	0.61
1,1-Dimethylcyclopentane	1.11	1.29	1.26	0.83	2.56	1.47
1,t2-Dimethylcyclopentane	4.72	5.35	4.93	4.77	1.20	1.24
1,c2-Dimethylcyclopentane	1.12	1.09	0.94	0.87	0.44	0.59
1,t3-Dimethylcyclopentane	2.22	2.59	2.34	1.97	2.52	1.35
1,c3-Dimethylcyclopentane	2.15	2.49	2.30	1.78	2.40	1.50
Toluene	4.23	3.81	5.55	3.61	0.00	1.99
2,2-Dimethylhexane	0.40	0.40	0.29	0.20	1.80	0.21
2,4-Dimethylhexane	4.53	3.64	3.23	4.44	2.73	0.53
2,5-Dimethylhexane	2.79	2.34	2.04	2.59	1.16	0.23
3,3-Dimethylhexane	0.87	0.77	0.66	0.79	1.44	0.16
2,2,3-Trimethylpentane	0.00	0.00	0.00	0.00	0.75	0.19
2,2,4-Trimethylpentane	0.03	0.09	0.06	0.02	0.00	0.00
2,3,4-Trimethylpentane	1.37	0.85	0.93	0.91	1.11	0.08
1,1,2-Trimethylcyclopentane	1.40	0.82	0.84	0.85	1.74	1.34
1,1,3-Trimethylcyclopentane	2.01	1.83	1.47	1.84	6.63	0.27
1,t2,c3-Trimethylcyclopentane	4.47	3.19	2.85	4.08	2.49	0.67
1,t2,c4-Trimethylcyclopentane	3.54	2.84	2.39	3.36	5.69	0.51

the flow rate used, this cold trap quantitatively retained all hydrocarbons which boiled below 114°C, including methane. A one and one-half hour flushing time of the sample at 120°C proved ample to release all of the hydrocarbons boiling below 114°C.

The closed U-tube containing the hydrocarbons was then heated in an oil bath at 140°C and the vapors were flushed into the GLC instrument. This instrument was equipped with a 400-foot (121.76 m), 0.02 inch (0.05 cm) I.D. column especially designed for the complete resolution of all the C_4 through C_7 and part of the C_8 hydrocarbons (Schwartz and Brasseaux 1963).

Table 13 shows the distribution of hydrocarbons boiling below 114°C that were isolated from Sample GM-S-101. Repeated samplings, although done with care, appear to result in a loss of volatile material. However, the isomer distribution in each of the carbon-number groups remains essentially the same. The distribution for two low API gravity, Gulf Coast, Tertiary oils is shown, also.

Comparison of the Organic Matter in Core 5 with Two Tertiary Crude Oils from the Gulf Coast Area

In order to show that the Challenger Knoll oil is somewhat like other Gulf Coast oils, compositional data for two Gulf Coast Tertiary crudes are shown. These crude oils are identified in Table 14.

TABLE 14
Identification of Oils Selected for Comparison with the Organic Matter in the Challenger Knoll Sample

Sample HA-0-56	Spindletop Field Jefferson County, Texas Texas Gulf Sulfur Gladys City No. 40 Open Hole 1013-21′
Sample HA-0-109	Stratton Ridge Field Brazoria County, Texas E. Cockrell, Jr. No. 3 Seaburn T.D. 5520′

Inasmuch as the Challenger Knoll oil had a high sulfur content, and since the only Gulf Coast Tertiary crudes with high sulfur appear to be associated with salt dome cap rock, a cap rock oil from Spindletop was chosen for one of the comparison oils. For contrast, the second comparison oil was a low-sulfur crude, and it had an API gravity similar to that of the Spindletop crude.

The compositions of these two crude oils are compared below with the Challenger Knoll oil. For additional and useful comparisons, the reader is referred to H. M. Smith's summary on the composition of petroleum (Smith, 1968).

The Spindletop cap rock oil and the Stratton Ridge petroleum have API gravities of 22.7 and 24.6 and sulfur contents of 2.1 and 0.51 per cent, respectively. The high sulfur content, 4.9 per cent, found in the Challenger Knoll core is not unusual for a cap rock oil.

All three oils as shown in Table 13 are characterized by a low relative concentration of paraffins and a high concentration of iso- and cyclo-paraffins in the fraction boiling below 114°C. The Challenger Knoll sample is particularly rich in cyclohexane and methylcyclohexane. A graphic comparison of the C_7 saturated hydrocarbons, shown in Figure 11, illustrates the similarity between the oils, particularly between the Challenger Knoll sample and the cap rock oil.

The *n*-alkane distribution from C_{20} to C_{35} shows that the Challenger Knoll oil does not display any predominance of molecules containing an odd number of carbon atoms. This is typical of most crude oils.

Volatility distributions for the two comparison oils, shown in Figures 12 and 13, differ from that for the Challenger Knoll oil, primarily in the lower amount of residue boiling above C_{35}. The two comparison oils contain about 10 per cent residue while the Challenger Knoll oil contains 44 per cent. However, this high value is not uncommon in low API gravity petroleum.

Conclusion

From a compositional point of view it is concluded that the organic material in Core 5, Leg 1, Site 2, is similar to naturally occurring petroleum of low API gravity and high sulfur content.

References

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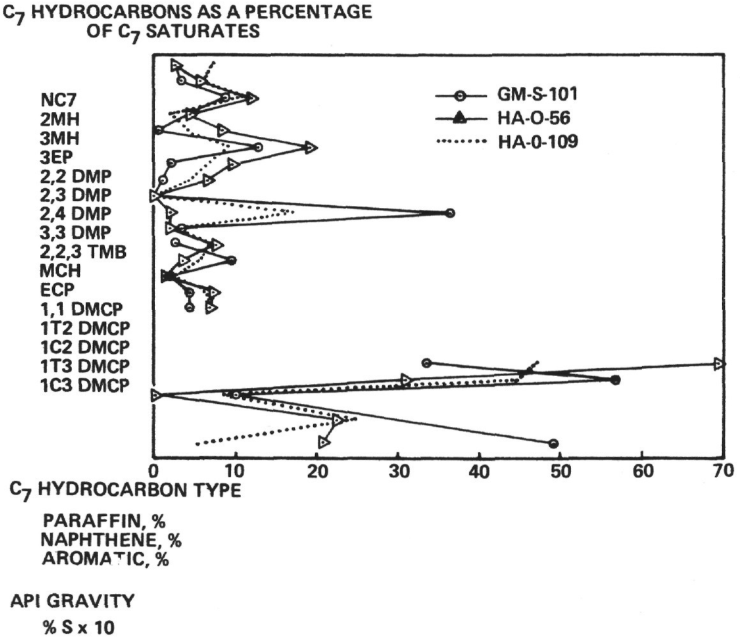

Figure 11. *Comparison of oil compositions.*

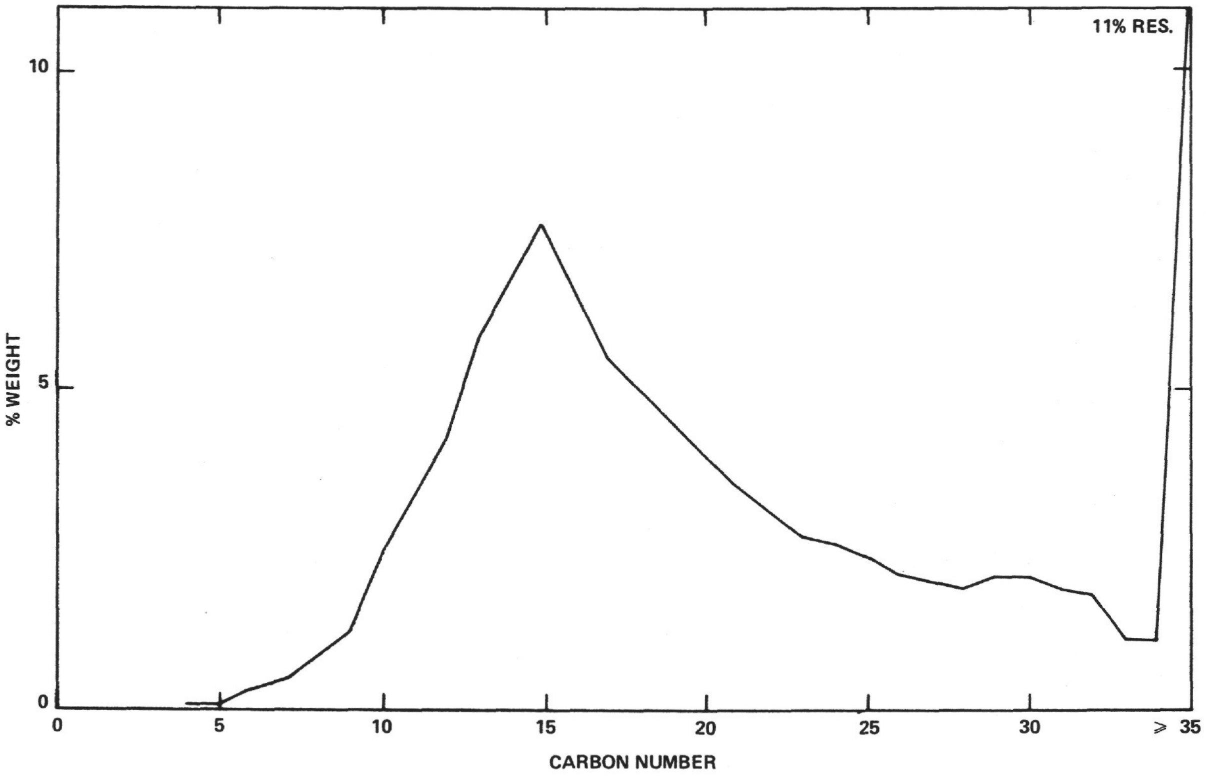

Figure 12. *Volatility distribution, HA-0-56.*

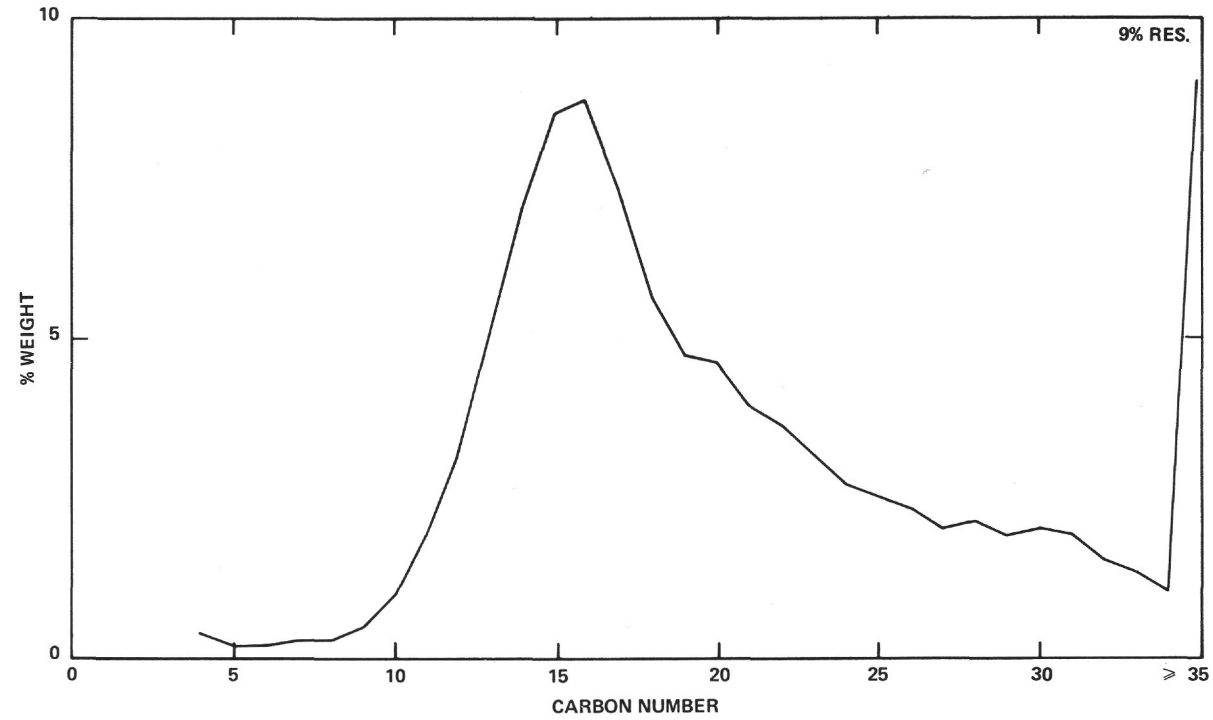

Figure 13. *Volatility distribution, HA-0-109.*

2.8 DATA AND DISCUSSION OF ANALYSES BY ESSO PRODUCTION RESEARCH COMPANY, INCLUDING C^{12}/C^{13} RATIOS (1.5.2)

Bruce Koons and P. H. Monaghan
Esso Production Research Company

Gas Chromatographic Analysis of C_4 Through C_{10} Hydrocarbons

Data

Pk. No.	Hydrocarbon	Normalized Weight Per Cent
1	*n*-Propane	0.14
2	Isobutane	1.53
3	*n*-Butane	0.34
	Neopentane	0.09
4	Isopentane	0.96
5	*n*-Pentane	0.12
6	2,2-Dimethylbutane	0.07
7,8	Cyclopentane	3.08
7,8	2,3-Dimethylbutane	0.41
9	2-Methylpentane	0.66
10	3-Methylpentane	1.90
11	*n*-Hexane	0.14
12	Methylcyclopentane	1.32
13	2,2-Dimethylpentane	0.10
14	2,4-Dimethylpentane	0.38
15	Benzene	0.49
16	3,3-Dimethylpentane	0.14
17	Cyclohexane	5.59
18	2-Methylhexane	0.52
19	2,3-Dimethylpentane	1.92
20	1,1-Dimethylcyclopentane	0.32
21	3-Methylhexane	1.32
22	1-t-3 Dimethylcyclopentane	0.71
23	1-c-3 Dimethylcyclopentane	1.28
23	3-Ethylpentane	
24	1-t-2 Dimethylcyclopentane	1.37
26	*n*-Heptane	0.13
27	1-c-2 Dimethylcyclopentane	0.21
	2,2-Dimethylhexane	0.06
28	1,1,3-Trimethylcyclopentane	0.45
29	Methylcyclohexane	5.60
30	2,5-Dimethylhexane	0.76
31	2,4-Dimethylhexane	1.10
32	Ethylcyclopentane	0.64
33	2,2,3-Trimethylpentane	0.02
34	1-t-2-c-4 Trimethylcyclopentane	0.80
35	3,3 Dimethylhexane	0.22
36	Toluene	0.63
36	1-t-2-c-3 Trimethylcyclopentane	1.06
37	2,3,4-Trimethylpentane	0.30
38	2,3,3-Trimethylpentane	1.03
39	1,1,2-Trimethylcyclopentane	0.77
40	2,3-Dimethylhexane	0.36
41	2-Methylheptane	0.61

Pk. No.	Hydrocarbon	Normalized Weight Per Cent
42	4-Methylheptane	0.55
43	3,4-Dimethylhexane	0.48
44	3-Methylheptane	1.59
45	1-c-2-t-4 Trimethylcyclopentane	0.04
46	2,2,5-Trimethylhexane	0.09
47	1-c-2-c-4 Trimethylcyclopentane	0.29
49	1-c-3 Dimethylcyclohexane	3.61
49	1-t-4 Dimethylcyclohexane	
50	1-Methyl-t-3 ethylcyclopentane	0.60
52	1-Methyl-t-2 ethylcyclopentane	1.70
53	1-Methyl-1-ethylcyclopentane	0.16
54	*n*-Octane	0.69
55	1-t-2 Dimethylcyclohexane	1.85
56	1-c-4 Dimethylcyclohexane	0.80
57	1,1-c-3-c-4 Tetramethylcyclopentane	0.30
58	2,2-Dimethylheptane	0.19
59	1-c-2 Dimethylcyclohexane	0.82
60	2,6-Dimethylheptane	2.95
61	*n*-Propylcyclopentane	1.68
62	2,4-Dimethylheptane	0.67
63	Ethylcyclohexane	2.89
	Ethylbenzene	1.70
64	2-Methyl-3-ethylhexane	4.00
66	(Cyclopentane)	0.79
67	(Cyclopentane)	0.12
68	*p*-Xylene	0.78
69	*m*-Xylene	1.08
70	1,1,3-Trimethylcyclohexane	3.72
71,72	3,3,4-Trimethylhexane	0.92
71,72	1-t-2-t-4 Trimethylcyclohexane	
73	1-c-3-t-5 Trimethylcyclohexane	0.13
74	2-Methyloctane	1.25
76	4-Methyloctane	1.18
77	(Cyclopentane)	0.89
78	3-Methyloctane	1.26
79,80	*o*-Xylene	1.83
79,80	(Cyclopentane)	
81	3,3,5-Trimethylheptane	0.29
82	(Cyclopentane)	0.36
83	(Cyclohexane)	1.02
84	(Isoparaffin)	0.42
85	(Cyclohexane)	0.46
87	1-t-2-t-3 Trimethylcyclohexane	0.38
86	Isobutylcyclopentane	0.12
88	1-t-2-c-4 Trimethylcyclohexane	1.57
89	Isopropylbenzene	1.12
90	*n*-Nonane	0.90
91	(Cyclopentane)	0.14
92	1-Methyl-c-3 ethylcyclohexane	0.14
93	1-Methyl-t-2 ethylcyclohexane	0.24
96	1-Methyl-c-4 ethylcyclohexane	0.71
95	1-Methyl-1-ethylcyclohexane	1.37
94	(Cyclopentane)	0.37
97	Isopropylcyclohexane	0.47
98	(Cyclohexane)	0.35
99	(Cyclohexane)	0.68
100	(Cyclohexane)	0.19
101	*n*-Propylbenzene	0.60
102	*n*-Propylcyclohexane	0.22
103	2,6-Dimethyloctane	4.63
104	1-Methyl-c-2 ethylcyclohexane	0.57
106	2-Methyl-3-ethylheptane	1.30

Method

A modification of the technique described by Dunton and Hunt (1962) was used for the analysis of the C_4 through C_{10} hydrocarbons in the core sample. One-half gram of core sample was weighed into a steel grinding capsule, and 0.5 milliliter of highly purified 1-tetradecene was added. A steel ball was added and the capsule was sealed. The capsule was vibrated in a Spex Mixer Mill for 15 minutes. This reduced the rock to a fine powder and released the hydrocarbons into the solvent. The sealed capsule was then centrifuged to force the rock particles to the bottom. The capsule lid was removed and 10 milliliters were drawn into a syringe and injected into a hot injection block which volatilized the fluid. The gases were then swept by helium into a prefractionator column (described by Martin and Winters, 1959) to retain the 1-tetradecene and heavier hydrocarbons and permit the C_4 through C_{10} hydrocarbons to go through. The latter were then analyzed on a 300 foot (91.44 m), 0.25 mm I. D., capillary column coated with squalane. A hydrogen flame ionization detector was used with the column. Other pertinent information on the gas chromatographic technique include the following:

Model:	Perkin-Elmer 226
Carrier Gas:	Helium
Flow Rates:	Hydrogen-10 ml/min; air-35 ml/min
Temperatures:	Column 40-110°C; Detector 135°C; Block 245°C.

The gas chromatographic trace is included (Figure 14); and, the peak numbers in the data table correspond to the numbered peaks on the gas chromatogram. The weight per cent values shown in the table are normalized to 100 per cent for the C_4 through C_{10} fraction of the oil. It is estimated that the C_4 through C_{10} fraction represents about 14 weight per cent of the total oil in the rocks.

References

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Martin, R. L., and Winters, J. C., 1959. *Anl. Chem.* **31,** 1954.

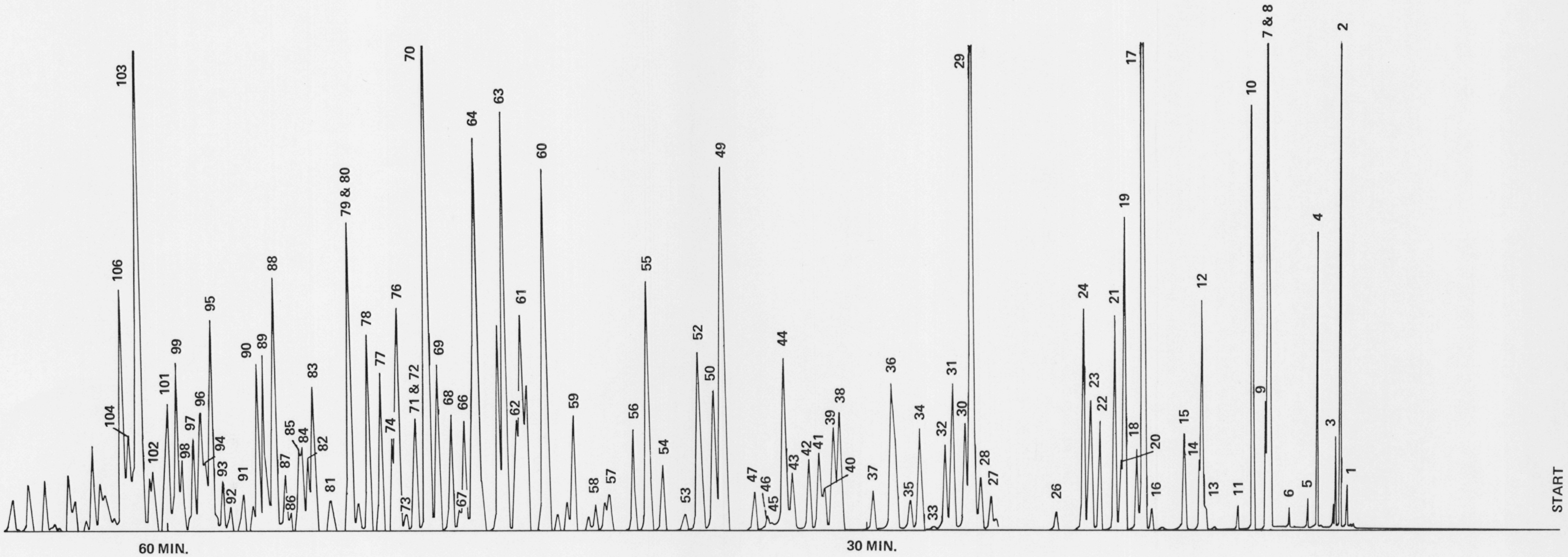

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Figure 14.

Separation of Higher Molecular Weight Components ($>C_{13}$) of Challenger Knoll Oil

Data

Fraction	Weight Per Cent of Oil
Saturated hydrocarbons ($>C_{13}$)	33%
Aromatic hydrocarbons ($>C_{13}$)	41
Polar NSO compounds	12
Asphaltenes	14

Method

The extracted oil,[1] dissolved in benzene, was chilled to 0°C, and the solvent stripped off by flowing purified nitrogen across the surface of the extract until the odor of benzene could not be detected. Forty milliliters of Matheson, Coleman and Bell Spectroquality normal pentane per gram of extract was added and allowed to stand for at least one hour. The precipitated asphaltenes were centrifuged, the *n*-pentane solution decanted, and the asphaltenes washed with two 10 milliliter portions of *n*-pentane. The *n*-pentane washings were combined with the original *n*-pentane solution and saved for elution chromatography, described in the following paragraphs. The precipitated and washed asphaltenes were weighed and calculated to represent 14 weight per cent of the stripped oil.

The combined pentane solution was cooled to 0°C and the solvent stripped off in the same manner as described earlier. Care was taken to prevent the introduction of water vapor into the stripping apparatus. The residue represented the stripped-deasphaltened oil.

Elution chromatography was used to separate the saturated hydrocarbons, aromatic hydrocarbons, and polar NSO compounds in the stripped-deasphaltened oil. A 0.9 to 1.0 centimeter I. D. by 45 centimeter glass column was fitted at the top with a 100 milliliter reservoir, and at the bottom with a straight bore Teflon stopcock. The column was packed wet in MCB *n*-pentane with a lower level of 10±0.2 gram Davison 28-200 mesh Grade 12 silica gel (activated at 150°C for at least 16 hours), and an upper level of 10±0.2 gram Alcoa F-20 alumina (activated at 400°C for at least 16 hours).

About 200 milligrams of stripped-deasphaltened oil, weighed to 0.1 milligram, was dissolved in 3 milliliter MCB *n*-pentane and added to the top of the *n*-pentane-wet column. Sixty additional milliliters of MCB *n*-pentane were added to the column to elute the saturated hydrocarbons. The eluate was chilled to 0°C and the *n*-pentane stripped off, as described earlier. The residue was weighed and recorded as saturated hydrocarbons.

After the *n*-pentane had been drained from the column so that the *n*-pentane level was at the top of the alumina bed, 200 milliliters of distilled Baker's analyzed benzene was added to the column to elute the aromatic hydrocarbons. The same stripping technique was used to remove the benzene. The residue was weighed and recorded as aromatic hydrocarbons.

That portion of the oil that remained on the alumina-silica gel column after *n*-pentane and benzene elution was called polar NSO compounds and was determined by difference in weight between the total charge to the column and the combined weights of the individual saturated and aromatic hydrocarbon fractions. Handling losses would be included in the polar NSO fraction, so the real value may tend to be lower than the reported value.

The four fractions (saturated hydrocarbons, aromatic hydrocarbons, polar NSO compounds, and asphaltenes) were normalized to 100 per cent, as shown in the preceding data table. Subsequent gas chromatographic analyses indicate that the stripping techniques described above remove the volatile components from the oil and that C_{13} is a very rough approximation of the cut-off point of the stripping. It should be realized, however, that this C_{13} value is a very rough average across the C_{11} to C_{15} fraction of the oil. Thus, some trace amounts of C_{11} hydrocarbons remain in the stripped oil, whereas most, but not all, of the C_{15} components remain in the stripped oil.

Compound Type Analysis of C_{13+} Saturated Hydrocarbons

Data

Elemental Formula	Wt %	Compound Type
C_nH_{2n+2}	32	Paraffin
C_nH_{2n}	35	Noncondensed naphthene
C_nH_{2n-2}	18	2-Ring naphthene
C_nH_{2n-4}	9	3-Ring naphthene
C_nH_{2n-6}	4	4-Ring naphthene
C_nH_{2n-8}	2	5-Ring naphthene
C_nH_{2n-10}	<1	6-Ring naphthene

Method

The procedure used for the compound type analysis of complex mixtures of saturated (paraffin-naphthene) hydrocarbons has been described by Lumpkin (1956).

A Consolidated Model 21-103 analytical mass spectrometer equipped with a high temperature inlet system

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[1] The rock extraction was carried out at Mobil laboratories and is described elsewhere in this report.

was employed to obtain the mass spectra of the $C_{13}+$ saturated hydrocarbon fraction of the Challenger Knoll oil.

The Lumpkin saturate calibration matrix was used with no modification and peak heights for fifty-five characteristic masses were determined. All calculations were done by computer.

Reference

Lumpkin, H. E., 1956. *Anl. Chem.* **28**, 1946.

Compound Type Analysis of C_{13+} Aromatic Hydrocarbons[1]

Data

Elemental Formula	Weight Per Cent	Typical Compound Type
C_nH_{2n-6}	7.3	Benzene
C_nH_{2n-8}	8.4	Naphthenobenzene
C_nH_{2n-10}	9.6	Dinaphthenobenzene
C_nH_{2n-12}	13.1	Naphthalene
C_nH_{2n-14}	7.4	Naphthenonaphthalene
C_nH_{2n-16}	7.4	Fluorene
C_nH_{2n-18}	7.2	Phenanthrene
C_nH_{2n-20}	6.1	Naphthenophenanthrene
C_nH_{2n-22}	3.7	Pyrene
C_nH_{2n-24}	1.2	Chrysene
C_nH_{2n-26} to C_nH_{2n-40}	4.7	Higher condensed aromatics
$C_nH_{2n-10}S$	6.6	Benzothiophene
$C_nH_{2n-12}S$	2.8	Naphthenobenzothiophene
$C_nH_{2n-14}S$	1.2	Dinaphthenobenzothiophene
$C_nH_{2n-16}S$	8.2	Dibenzothiophene
$C_nH_{2n-18}S$	1.2	Naphthenodibenzothiophene
$C_nH_{2n-20}S$	0.9	Fluorenothiophene
$C_nH_{2n-22}S$	0.7	Phenanthrenothiophene
$C_nH_{2n-24}S$	0.3	Naphthenophenanthrenothiophene
$C_nH_{2n-26}S$, $C_nH_{2n-28}S$	0.3	Higher condensed sulfur heterocyclics
$C_nH_{2n-6}O$	0.2	Naphthenofuran
$C_nH_{2n-16}O$	0.4	Dibenzofuran
$C_nH_{2n-18}O$	0.2	Naphthenodibenzofuran
$C_nH_{2n-22}O$	0.1	Phenanthrenofuran
$C_nH_{2n-24}O$	0.2	
$C_nH_{2n-26}O$	0.1	Naphthenophenanthrenofuran
C_nH_{2n-2}, C_nH_{2n-4}	0.5	Saturates
	100.0%	

Method

The procedure used for the analysis of complex mixtures of aromatic compounds by high-resolution mass spectrometry at low-ionizing voltages has been described by Johnson and Aczel (1967).

The apparatus used was an Associated Electrical Industries Ltd., MS-9 high-resolution instrument. This is a double focusing mass spectrometer, of the Nier-Johnson geometry. The output of the instrument was recorded with a Minneapolis-Honeywell UV visicorder.

The procedure reported here has been used for the detailed characterization of a wide variety of petroleum materials, as reported by Johnson and Aczel (1967). Sensitivity data for the aromatic nuclei were derived from experimental data, whenever available, and by extrapolation techniques assuming that the nuclear sensitivities are directly proportional to the number of double bonds in the structure. Most of the experimental sensitivities were those obtained previously on a Consolidated Electrodynamics Company Model 21-103C spectrometer, as reported by Lumpkin and Aczel (1964). It has been shown in Esso Research and Engineering Company laboratories and by Reid, *et al.* (1964) that the relative sensitivities on the two instruments are interchangeable.

All calculations were carried out on a computer. The data output includes the weight per cent corresponding to each individual peak and the weight per cent of each compound type, shown in the data table. The coefficient of variation on replicate analyses is about 10 per cent of the amount present.

References

Johnson, B. H., and Aczel, T., 1967. *Anl. Chem.* **39**, 682.

Lumpkin, H. E., and Aczel, T., 1964. *Anl. Chem.* **36**, 181.

Reid, W. K., Mead, W. L., and Bowen, K. M., 1964. Paper presented at the Institute of Petroleum/ASTM Spectrometry Symposium, Paris, 1964.

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[1] Mass spectrometry analysis performed at Esso Research and Engineering Company, Baytown, Texas.

Gas Chromatographic Analyses of Saturated Hydrocarbons (C_{13+}) and Isoparaffins-Naphthenes

Data

Compound Type	Weight Per Cent in Saturate Fraction
n-Paraffins ($C_{13}+$)	12%
Isoprenoid isoparaffins ($C_{14}+$)	2
Other isoparaffins plus naphthenes	86
	100%

Method

The saturated hydrocarbon fraction was analyzed by gas chromatography. Following are the conditions used for the analysis:

Instrument:	Varian-Aerograph Model 204-B
Column:	1/8 inch O.D., 22 feet, stainless steel
Packing:	Eutectic ($NaNO_3$, KNO_3, $LiNO_3$), m.p. 150°C, on Chromosorb P, 60-80 mesh, obtained from Microtek.
Detector:	Flame ionization
Column Temperature:	Isothermal 160°C for 2 minutes, 12°/min for 13 minutes, isothermal 316°C for 10 or more minutes.
Detector Temperature:	275°C
Injector Temperature:	300°C
Flow Rates:	Helium-14 ml/min; Hydrogen-25 ml/min; Air-35 ml/min.

The use of this eutectic for a column packing has been described by Hanneman *et al.* (1960). The gas chromatographic trace for the analysis of the saturated hydrocarbon fraction is shown (Figure 15). Peaks corresponding to the normal paraffins between C_{12} and C_{25} are marked, as well as the isoprenoid isoparaffins farnesane, C_{16}, C_{18}, pristane, and phytane.

The saturated hydrocarbons were treated with Linde 5Å Molecular Sieve to remove the normal paraffins. One hundred and seventy-two milligrams of the saturate fraction were dissolved in 10 milliliters of distilled Baker's Analyzed benzene; 3.8 grams of 5Å sieve pellets, activated at 400°C for 24 hours, were added and the mixture boiled under total reflux for 16 hours. The sieve pellets were filtered from the hot benzene solution on a glass fritted disc, and washed with two 20 milliliter portions of hot benzene. The filtrate and washings were transferred to a tared container and the benzene stripped off with dry nitrogen. One hundred

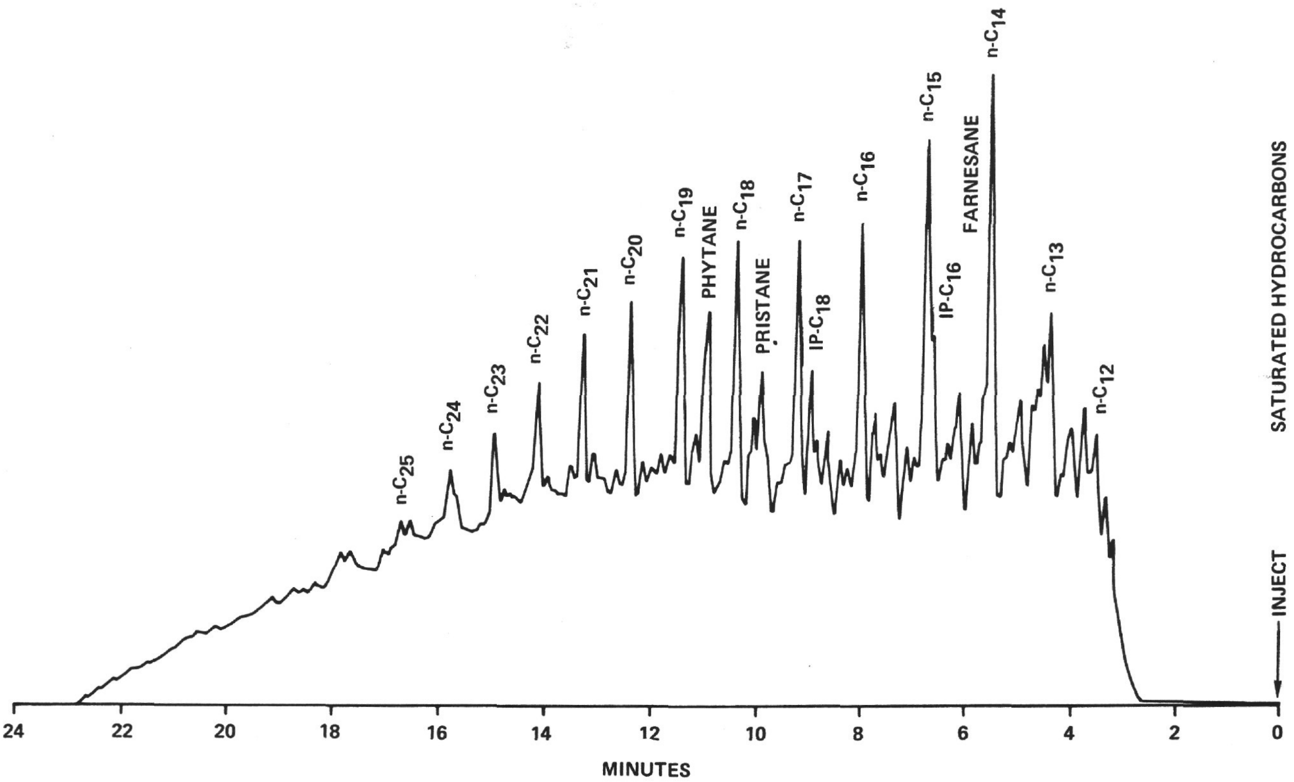

Figure 15. *Gas chromatographic trace for analysis of saturated hydrocarbon fraction.*

and forty-seven milligrams of isoparaffins plus naphthenes were recovered, representing 86 per cent of the total saturate fraction.

The 5Å sieve pellets were transferred to a Nalgene beaker, to which was added 50 milliliters of 16 per cent hydrogen fluoride solution and 10 milliliters of Phillips research grade iso-octane. The reaction mixture was stirred vigorously with a Nalgene stirring rod and cooled in an ice bath when the reaction became too vigorous. After the sieve pellets were completely decomposed and the reaction mixture cooled to room temperature, the iso-octane layer was separated from the aqueous layer and saved. The aqueous layer was then washed with three additional 10 milliliter portions of iso-octane. The washings were combined with the original iso-octane extract and the solvent removed as described above. Twenty milligrams of normal paraffins were collected, representing 12 per cent of the total saturate fraction. Thus, the loss in weight during the sieving process amounted to 2 per cent of the total saturate fraction.

The isoparaffin-naphthene fraction was analyzed by gas chromatography, with the operating conditions identical to those used for the total saturated hydrocarbons. The gas chromatographic trace is shown (Figure 16). It should be noted that the normal paraffins were removed completely, and the isoprenoid isoparaffins remained in the sample (farnesane, C_{16}, C_{18}, pristane, and phytane). A rough estimate of the isoprenoid isoparaffin content was made by planimetering the area under the isoprenoid peaks and comparing the area obtained with the area of the remainder of the chromatogram. This gave a value of 2 per cent isoprenoid isoparaffins and 98 per cent other isoparaffins plus naphthenes. It is readily admitted, however, that this analysis is only a rough approximation.

By combining these two analyses (normal paraffin content by 5Å sieving and isoprenoid isoparaffin content by planimetering), the data reported in the preceding table was obtained.

Reference

Hanneman, W. W., Spencer, C. F., and Johnson, J. F., 1960. *Anl. Chem.* **32**, 1386.

Carbon Isotope Data and Methods

Data

	$\delta C^{13}/C^{12}$
Total extract (C_{13+})	-26.6
Hexane-soluble extract (C_{13+})	-26.6
Asphaltenes (hexane-insoluble, benzene-soluble)	-26.8
Saturated hydrocarbons (C_{13+})	-26.5
Normal paraffins (C_{13+})	-27.0
Isoparaffins plus naphthenes (C_{13+})	-26.4
Aromatic hydrocarbons (C_{13+})	-26.8
Polar NSO compounds (C_{13+})	-26.5

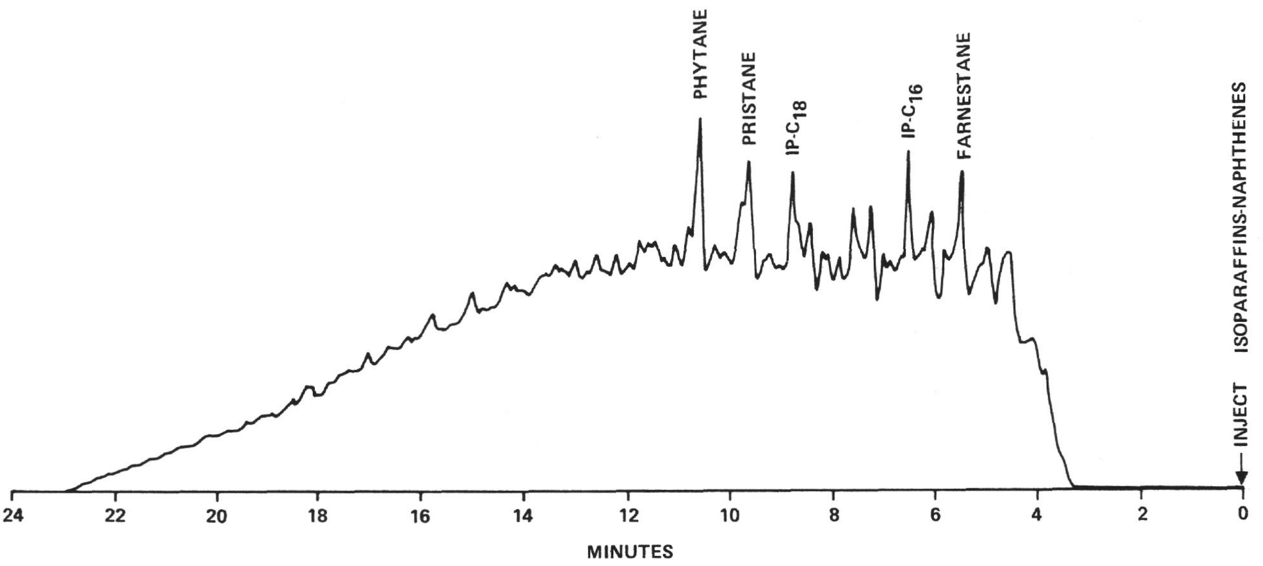

Figure 16. *Gas chromatographic trace for isoparaffin-naphthene fraction.*

Method

The experimental procedures have been described by Eckelmann, *et al.* (1962).

The samples were combusted over copper oxide at approximately 800°C in the presence of oxygen in a manner similar to that reported by Craig (1953) and purified by passing the carbon dioxide gas over a dry ice-Freon 11 trap.

The purified carbon dioxide samples were analyzed in a 60 degree, sector-type mass spectrometer similar to that described by Nier (1947) and Nier *et al.* (1962).

The mass spectrometric analyses are reported as per mil deviations (δ) from the C^{13}/C^{12} ratio of the Cretaceous belemnite, *Belemnitella americana,* from the Peedee Formation of South Carolina. In practice, a commercial lubricating oil with an assigned value of -29.40 per mil relative to the Peedee belemnite was used as the laboratory standard. This lube oil was the National Bureau of Standards Isotope Standard Number 22, supplied by Silverman.[1]

δ in per mil (°/oo)

$$= \frac{[C^{13}/C^{12}\ (\text{Sample}) - C^{13}/C^{12}\ (\text{Standard})] \times 1{,}000}{[C^{13}/C^{12}\ (\text{Standard})]}$$

Appropriate corrections for carbon dioxide background in source (1.0017), mixing of sample and standard due to leakage (1.0000), and tailing of the mass 44 peak under the mass 45 peak (1.0050) were made; and, the corrected per mil values were calculated using the equations derived by Craig (1957).

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Analyses of the Challenger Knoll Oil: Implications and Comparisons

The analysis of the C_4 through C_{10} hydrocarbons in the Challenger Knoll oil identify it as a natural petroleum, but of a rather unusual type. The estimated total quantity of these lighter hydrocarbons in the oil is about 14 per cent, based on Esso data. Shell's data indicates an even lower amount, about 5 per cent. Smith *et al.* (1959) have reported ranges of naphtha contents (approximately equivalent to the C_4 through C_{10} fraction) for several oil-producing areas in the U. S., including Gulf Coast Tertiary, California Tertiary, West Texas Permian, Mid-continent Cretaceous and Paleozoic, Michigan Devonian, and Pennsylvania Devonian. The Challenger Knoll oil is definitely on the lean side for naphtha content, most resembling some of the Gulf Coast and California Tertiary oils. It is possible that the Challenger Knoll oil may have originally contained a greater quantity of these C_4 through C_{10} hydrocarbons, but that some were lost when the core was brought to the surface, and during handling between the time it was taken aboard ship and the time it was analyzed in the laboratory. If the naphtha content of the Challenger Knoll oil is truly quite low, this would suggest a rather immature petroleum, one that had not undergone appreciable chemical transformation. Silverman (1964) has presented good evidence, based on carbon isotope studies, that the lighter hydrocarbons in petroleum arise through decomposition of more complex compounds. He calls on a natural maturation process to bring about this decomposition.

There are several very interesting observations that can be made concerning the individual hydrocarbon components in this C_4 through C_{10} fraction of the Challenger Knoll oil. Ten hydrocarbons, including: methylcyclohexane, cyclohexane, 2,6-dimethyloctane, 2-methyl-3-ethylhexane, 1,1,3-trimethylcyclohexane, 1-t-4-dimethylcyclohexane, 1-c-3-dimethylcyclohexane, cyclopentane, 2,6-dimethylheptane, and ethylcyclohexane, make up some 36 per cent of the total hydrocarbons in this C_4 through C_{10} range. This is rather remarkable when it is considered that over 200 individual hydrocarbon structures could theoretically be present in this fraction of the oil. Hydrocarbon types that dominate in the Challenger C_4 through C_{10} fraction are the isoprenoid isoparaffins and the cyclohexanes. The normal paraffin and the aromatic hydrocarbon contents are relatively low. Interestingly enough, Reznikov (1967) has found on studies of Russian crude oils that naphthene contents in this same carbon number range seem to relate to the chemical conversion that an individual oil has undergone. High naphthenes represent oils that have undergone little alteration.

The chemical structures of the ten most abundant hydrocarbons appear most related to terpenoid precursors, either cyclic or acyclic, such as described by Mair *et al.* (1966, 1967). These precursor compounds contain the repeating isopentanyl and six carbon ring structures found in many of the more abundant Challenger Knoll oil light hydrocarbons.

If the light hydrocarbon composition of the Challenger Knoll oil is compared with the light hydrocarbon data published by Martin *et al.* (1963) on eighteen crude

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[1] California Research Corporation

oils of quite varying geological histories, the following observations can be made:

1. The Challenger Knoll oil most resembles the Middle East Wafra oil, reservoired in a Tertiary carbonate formation. Both oils are high in cyclohexanes and branched paraffins and low in *n*-paraffins and aromatics.

2. The Challenger Knoll oil shows a predominance of cyclohexane types over cyclopentane types. Martin *et al.* (1963) have suggested that a high cyclohexanes to cyclopentanes ratio may indicate either a non-marine source or a relatively young crude. The latter explanation seems to best fit the Challenger Knoll oil.

The analysis of the higher molecular weight components of the Challenger Knoll oil also show it to be a true petroleum, but of rather unusual composition. The asphaltene content is rather high, 14 per cent. Erdman (1962) has reported asphaltene contents for 13 crude oils of widely different geologic histories. Only two of the oils have comparable asphaltene contents: Boscan (Venezuela) Cretaceous (18 per cent), and the Athabasca (Canada) Cretaceous (19 per cent).

The aromatic hydrocarbon content of the higher molecular weight components is rather high (41 per cent). This contrasts rather markedly with the C_4 through C_{10} fraction, where the aromatic content is estimated to be only about 8 per cent.

The compound type analysis of the saturated hydrocarbons show a predominance of paraffins and 1- and 2-ring naphthenes. The higher condensed ring saturates (3 through 6) are relatively low in quantity. Steranes and triterpanes are present only in very minor amounts.

The compound type analysis of the aromatic hydrocarbons also show a predominance of 1- and 2-ring aromatics over the higher condensed ring compounds. An unusually large amount of sulfur-containing compounds, particularly benzothiophenes and dibenzothiophenes, eluted with the aromatic hydrocarbons. However, since this oil was known to contain a high amount of organic sulfur, this is not surprising.

The gas chromatographic analyses of the C_{13+} saturated hydrocarbons before and after removal of the *n*-paraffins by molecular sieving revealed some additional, interesting information about the Challenger Knoll oil. The normal paraffins, which were very minor components in the lower boiling fraction (C_4-through C_{10}) of the oil, are moderately abundant in the C_{14} through C_{24} range, and then diminish quite rapidly after C_{24}. There is little if any predominance of either odd- or even-numbered *n*-paraffins, as has been noted in some petroleums. The carbon number range for the Challenger Knoll *n*-paraffins, C_{14} through C_{24}, is about the same range as that for the straight-chain fatty acids found in animal and plant fats (glycerides). This might indicate that the fats are the precursors for the *n*-paraffins. However, straight chain fatty acids found in fats usually display a very strong preference for an even number of carbon atoms, and the Challenger Knoll *n*-paraffins show no preference, neither even nor odd.

The isoprenoid isoparaffins: farnesane, C_{16}, C_{18}, pristane, and phytane appear to be present in the Challenger Knoll oil. The identifications are based only on retention times and are not absolute identifications. The isoprenoid isoparaffin peaks are labeled on both chromatograms, before and after molecular sieving. Phytane, the C_{20} compound, appears to be the most abundant. From the chromatograms a very rough estimate was made of the pristane/phytane ratio, which is 0.7. Martin *et al.* (1963) have published pristane and phytane contents for 17 different petroleums of quite varying geological histories. The average pristane/phytane ratio for these oils is 1.3, with a range from 0.6 to 2.2. It is quite interesting to note that among the 17 oils, the three oils with the lowest pristane/phytane ratios (Darius - 0.7, Lee Harrison - 0.6, and Wafra - 0.7) also have the highest sulfur contents (2.7, 3.2, and 4.8, respectively). The Challenger Knoll oil certainly fits in with these three oils. Age in this case may not be a factor since the three oils were produced from Cretaceous, Permian, and Tertiary age reservoirs, respectively. The producing formations in all three cases are identified as marine carbonates, which matches the Challenger Knoll occurrence.

The carbon isotope data on the total oil and on fractions of the oil show some interesting results. The C^{13}/C^{12} ratio on the total oil is -26.6 °/oo, relative to the Peedee belemnite standard. Silverman (1964) has published C^{13}/C^{12} ratio ranges of natural carbonaceous materials. He lists the range for petroleums believed to be derived from organic matter deposited in marine environments as -20 to -29°/oo. The Challenger Knoll oil falls in this range. Feely and Kulp (1957) have published C^{13}/C^{12} data on two Gulf Coast cap rock crudes from Boling Dome and Lake Washington which average out -26.3°/oo and -25.6°/oo. These values are similar to those obtained on the Challenger Knoll oil.

The most surprising thing about the carbon isotope data on the fractions is the rather close agreement between the saturated hydrocarbons (-26.5°/oo), aromatic hydrocarbons (-26.8°/oo), polar NSO compounds (-26.5°/oo), and asphaltenes (-26.8°/oo). Since the standard deviation for the individual analysis is 0.1°/oo, this means essentially there is no significant difference between the various fractions. One possible explanation for this observation is that the Challenger Knoll oil is a very immature one and that petroleum alteration reactions, such as those described by Silverman (1964), have not proceeded far enough to fractionate the carbon isotopes between the different types of hydrocarbons. The similarity in values for the different fractions also seems to support the hypothesis that all the fractions are derived from the same type of source material, such as the lipid fraction of organisms.

The only fraction of the Challenger Knoll oil that is slightly enriched in carbon-12 is the *n*-paraffin fraction (-27.0°/∘∘). This observation agrees with findings by Silverman and Epstein (1958) on waxes separated from four different crude oils, in which they obtained 0.2 to 0.9°/∘∘ enrichment of carbon-12 in the wax fractions.

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Feely, H. W., and Kulp, J. L., 1957. *Bull. Am. Assoc. Petrol. Geologists.* **41**, 1802.

Silverman, S. R., and Epstein, S., 1958. *Bull. Am. Assoc. Petrol. Geologists.* **42**, 998.

2.9 PETROLEUM ACIDS (1.5.2.2)

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Approximately 528 grams (25 per cent) of the total benzene extract of Core 5-1, containing 11.5 grams of oil, was extracted with an equal volume of 0.1 normal potassium hydroxide to recover the acidic fraction. The extracted benzene solution of the oil was washed repeatedly with distilled water to remove residual alkali and these washings were added to the alkaline solution.

The alkaline solution was washed three times with about 10 per cent (by volume) of hexane to remove any oil that may have been carried over with the alkali. The alkaline solution was then acidified to $< p\mathrm{H}\ 3$ with hydrogen chloride and extracted twice with hexane to recover the petroleum acids.

The petroleum acid fraction, dried *in vacuo,* weighed 33.6 milligrams equivalent to 0.292 per cent by weight of the oil sample. An infrared spectrum of the petroleum acids dissolved in carbon disulfide gave a spectrum characteristic of a composite of naphthenic acids extracted from crude oils (see Figure 17). The concentration of petroleum acids in oil from the Challenger (Sigsbee) Knoll may be compared with the concentration of petroleum acids in eight Tertiary oils from the Texas Gulf Coast area, analyzed by Mobil's Field Research Laboratory. The concentrations ranged from 0.0015 to 0.0396 per cent, with an average of 0.018 per cent.

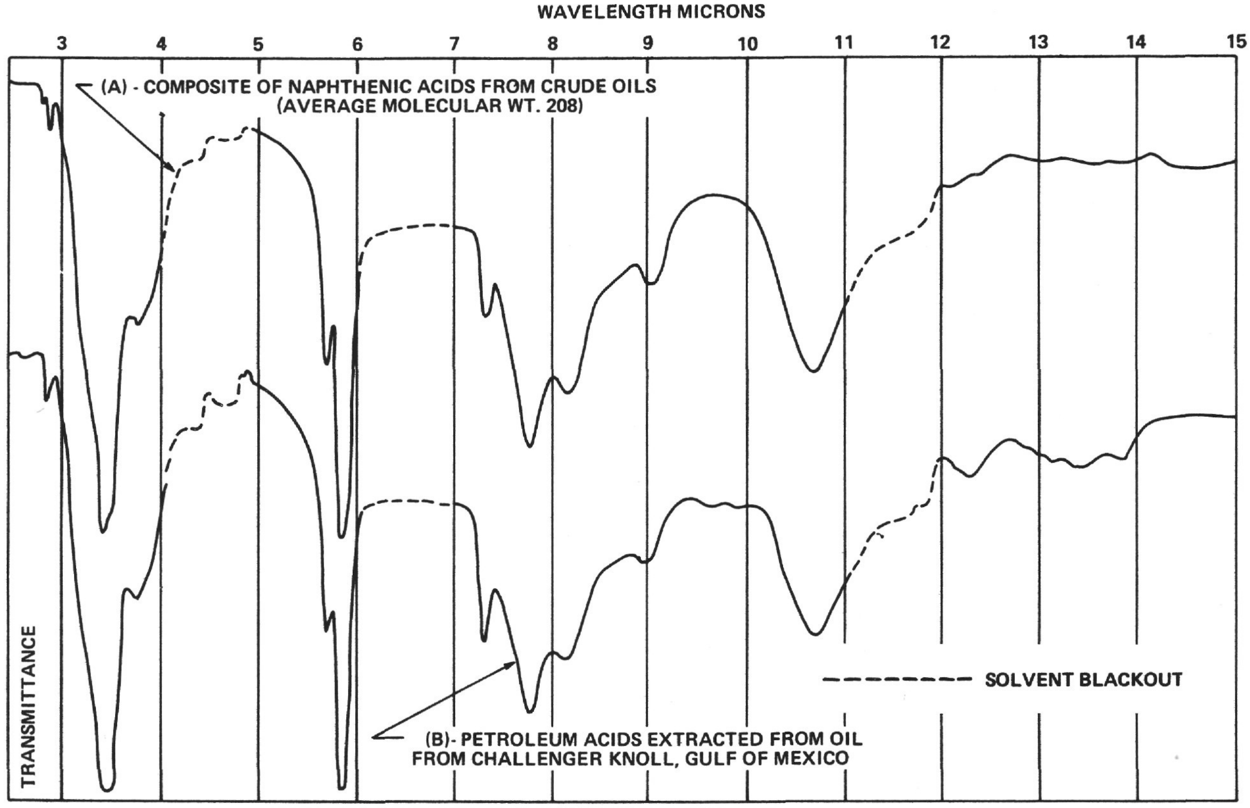

Figure 17. *Infrared spectrum of petroleum acids.*

2.10 SULFUR IN BENZENE EXTRACT OF CORE 5-1 (CHALLENGER KNOLL, GULF OF MEXICO)

(1.5.2.4)

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Mobil Research and Development Corporation, Dallas Texas

Results

Analytical results for sulfur in the benzene extract of Core 5-1 and of the solvent-free oil from the extract are summarized in Table 15. Organic sulfur and free sulfur (elemental sulfur) were determined individually because appreciable amounts of free sulfur were observed in the adjacent core section. The oil obtained by careful evaporation of the benzene was found to contain 3.75 weight per cent organic sulfur. Free sulfur in the oil containing core was found to be only 0.041 weight per cent which is surprisingly low compared to about 19 per cent found in the adjacent section Core 5-2. The distribution of this free sulfur between that dissolved in the oil and that existing as crystalline sulfur in the natural environment is not known. However, in the extract residue the free sulfur is dissolved in the oil and amounts to 1.24 weight per cent of the oil. Total sulfur in the extracted oil is therefore 4.98 weight per cent from the sum of our determinations of organic and free sulfur. This value was confirmed by direct determinations of total sulfur in the extract residue (solvent-free oil) by Shell Development Co. They report 4.90 and 4.97 weight per cent total sulfur for two separate determinations.

It is the authors opinion that the sulfur content of the Challenger Knoll oil should be reported as the organic sulfur content, i.e. 3.74 per cent organic sulfur, because the extent to which the free sulfur is dissolved in the oil in the natural environment is not known. Details are given in notes to Table 15 and comments on analytical methods are given under appropriate headings below.

Analyses and Methods

Sample

The sample used for sulfur analyses was a 4.97 weight per cent portion of the entire core extract (105.6 grams of the 2123 gram total). The extraction was made with a benzene-methanol mixture but the methanol was subsequently removed by water washing. The extract as received was essentially benzene and dissolved oil

TABLE 15

Summary of Sulfur Analyses[a]

Form of Sulfur	Weight Per Cent in Original Extract	Grams in Total Extract[b]	Weight Per Cent in Oil[c]	Parts per Million in Core[d]
Organic Sulfur	0.0810	1.72 ± 0.02	*3.74* ± 0.02	1243
Free Sulfur (S°)	*0.0266* ± 0.0007	0.57 ± 0.02	(1.24) ± 0.04[g]	412
Volatile Sulfur in Solvent[e]	*0.0036* ± 0.0003	0.07 ± 0.001	---	---
Sum	0.1112	2.36	(4.98) ± 0.04[h]	1655
Total determined on original extract[f]	*0.11* ± 0.02	---	---	---
Total determined on solvent-free oil	---	---	*4.94* ± 0.04[i]	---

[a] Original analytical data are in italics.
[b] Total extract was 2123 grams.
[c] Total oil recovered was 45.90 grams.
[d] Based on weight of dry core after extraction (1384 grams).
[e] Determined by Lamp method at Mobil Paulsboro Laboratory on a large sample of benzene used as extraction solvent. This volatile sulfur is assumed to be traces of thiophene in benzene and to be removed from the oil during evaporation to remove benzene.
[f] Single determination on small sample by ASTM Method D-129-60. The method is not sufficiently accurate at this low sulfur content and sample size for a good mass balance check.
[g] Data does not allow distribution of free sulfur between that dissolved in oil and that present as free element in solid phase.
[h] Includes free sulfur extracted from core which, however, cannot be assumed to be dissolved in the oil in natural environment.
[i] Average of two determinations reported by Shell Development Co. in Section 2-7.

saturated with water. The solvent was partially evaporated and the volume adjusted to exactly 100 milliliters. This adjusted extract is noted as "AE" during analyses and results are computed to the original extract (noted "OE").

Free Sulfur

Dissolved elemental sulfur (S°) was determined on aliquots of AE by a modification of the colorimetric method of Bartlett and Skoog. Direct application of the method to the extract was not satisfactory because of precipitation of asphaltic components in the polar solvent system. This interference due to turbidity could not be removed by filtration or centrifugation. A satisfactory sample was prepared by chromatography of AE on alumina containing two per cent water, using heptane to elute the free sulfur and non-interferring hydrocarbons. Three determinations on the same sample gave the following results:

Free Sulfur Concentration

Run No.	mg S°/liter of AE	mg S°/gram of OE
1	274	0.259
2	287	0.272
3	282	0.267
mean	281 ± 7	0.266 ± .007

Total free sulfur in OE is calculated as follows:

$$100 \text{ ml AE} = 0.0281 \text{ g } S^\circ = 4.97 \text{ wt \% of total OE}$$

$$\text{Total } S^\circ = (100/4.97)\ (0.0281 \text{ g } S^\circ) = 0.565 \text{ g } S^\circ$$

or

$$\text{Total } S^\circ = 2123 \text{ g OE} \times \frac{0.266 \times 10^{-3} \text{ g } S^\circ}{1.00 \text{ g OE}} = 0.565 \text{ g } S^\circ$$

Evaluation of errors indicates that results should be reported as:

$$\text{Total free sulfur } (S^\circ) = 0.57 \pm 0.02 \text{ grams}$$

Organic Sulfur in Oil

Free sulfur was removed from an aliquot of AE by reaction with sodium cyanide in a methanolic solvent system. The reaction

$$S^\circ + Na^+CN^- \quad Na^+SCN^-$$

is quantitative and does not affect organic sulfur compounds or other normal oil components.[1] The reaction product, sodium thiocyanate, was removed together with the methanol and excess sodium cyanide by washing with water. Benzene was then evaporated to obtain solvent-free oil, evaporated to constant weight at 40°C and 1-2 millimeters mercury. Sulfur content of the solvent-free oil was determined by the oxygen-bomb combustion method (ASTM Method D-129-60). Duplicate determinations gave 3.75 and 3.73 weight per cent sulfur (mean: 3.74 ± 0.02).

From the aliquots of AE used and the weights of solvent-free oil, the oil content of the total extract (free of S°) was calculated to be 45.99 and 45.81 grams (mean: 45.90 grams).

Total organic sulfur in oil is calculated:

$$\text{Total S in oil} = \frac{3.74 \text{ S}}{100 \text{ g oil}} \times 45.90 \text{ g oil} = 1.72 \text{ g S}$$

Total Sulfur in Original Extract

An approximate value for total sulfur in the original extract was determined by the oxygen-bomb combustion method (ASTM Method D-129-60) on a small portion of AE. Combustion of 1.00 milliliter (0.8728 gram) of AE gave 8.65 milligrams of barium sulfate (corrected for blank of 0.65 milligram on reagents) which corresponds to 0.136 weight per cent S in AE:

$$\% \text{ S} = \frac{0.00865 \times 13.73}{0.8728} = 0.136 \text{ wt \% S in AE}$$

Per cent sulfur in OE is calculated as follows:

$$\% \text{ S (OE)} = \frac{100 \text{ g OE}}{105.6 \text{ g OE}} \times \frac{100 \text{ ml AE}}{} \times \frac{0.8728 \text{ g AE}}{1.00 \text{ ml AE}} \times \frac{0.136 \text{ g S}}{100 \text{ g AE}} = 0.112 \text{ wt \% S in OE.}$$

Although this value agrees very well with the sums of determined components (Table 15), the value is of low accuracy because of the low sulfur content and small sample size and does not allow a good mass balance check irrespective of the apparent agreement.

Reference

Bartlett and Skoog, 1954. *Anl. Chem.* **26**, 1008.

2.11 HYDROCARBON GROUP TYPE ANALYSIS
(1.5.2.6)

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Mobil Research & Development Corporation
Paulsboro, New Jersey

This report described the work done by Mobil Research and Development Corporation at the Paulsboro and Dallas Laboratories. Low resolution mass spectrometry

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[1] If present, organic polysulfides ($R\text{-}S_x\text{-}R$) would be converted to organic disulfides ($R\text{-}S_2\text{-}R$) resulting in removal of sulfur atoms in excess of two per molecule of polysulfide. This sulfur, however, would have been determined already with the "truly free" elemental sulfur in the previous determination for free sulfur.

and gradient elution chromatography (GEC) were the principal techniques used at the Paulsboro Laboratory to characterize the organic matter from the core, which, it was concluded, resembles a high sulfur petroleum. Silica gel chromatography was used at the Dallas Laboratory for a gross separation into saturated, aromatic and asphaltic fractions giving results shown in Table 1 (Section 1).

At the Dallas Laboratory a measured portion of the oil dissolved in benzene was stabilized by forced evaporation of the solvent under a stream of nitrogen at 40°C. After removal of solvent the sample was weighed. These steps were repeated until no further loss of weight occurred. Mass spectrometer data have indicated that these stripping techniques remove volatile components from the oil and that C_{18} is a rough approximation of the cut-off point of the stripping. Although this C_{18} valve is a rough average across the C_{16} to C_{20} fraction of the oil, the method gives a reproducible fraction from any individual oil.

The stabilized oil residue was dissolved and chromatographed on activated silica gel by using, in sequence, as eluting agents: *n*-heptane, carbon tetrachloride, benzene, and methanol. The *n*-heptane fraction (F-1) contained the saturated hydrocarbons which were present. The carbon tetrachloride fraction (F-2) and the benzene fraction (F-3) were predominantly aromatic hydrocarbons although some oxygen-bearing impurities were present. The methanol fraction (F-4) was composed of asphaltic (hetero) compounds. The eluting solvents were removed by forced evaporation at 40°C, and the amount of residue in each of the fractions was determined by weight. Infrared spectra were obtained for each of the chromatographic fractions dissolved in carbon disulfide in order to characterize the material and observe the purity of the fractions. The solvents were carefully distilled to contain less than 0.2 micrograms per milliliter of impurities that would be recovered with the sample and eluates. The silica gel was 100-200 mesh, grade 923, Davison Company silica gel which was activated prior to use at 425°C for 6 hours. The chromatographic columns (10 millimeter I.D. by 360 millimeters long) contained 9 grams of the freshly activated silica gel. Column charges were adjusted to contain not more than 20 milligrams of asphaltic materials, so as not to exceed the retention capacity of the silica gel.

The sample used for hydrocarbon analysis at Paulsboro was the sample which was previously extracted with 0.1 normal potassium hydroxide to recover petroleum acids (see Section 2.9). This treatment should not affect the hydrocarbons, but could remove some acidic sulfur compounds (thiols) and possibly part of the free sulfur.

Gradient elution chromatography was used primarily to prepare fractions of reduced molecular complexity which would be amenable to existing mass spectrometric methods used to analyze petroleum mixtures.

The results are summarized as follows. A portion of the sample as received was stripped of benzene in a small distillation column and the residue was stabilized against appreciable weight loss by blowing with nitrogen. Elemental analysis of the oil residue indicated 4.62 per cent sulfur and 0.28 per cent nitrogen. Gradient elution chromatography separated the oil into a non-aromatic fraction and eight aromatic fractions representing 26.3 and 58.4 weight per cent of the oil, respectively. A final fraction composed of the asphaltene components was not eluted from the column, but comprised 15.3 per cent of the sample by difference.

The analysis by mass spectrometry of the non-aromatic and six of the aromatic fractions, which combined represent 66.8 per cent of the sample, are given in Tables 16 and 17, respectively. The remaining fractions (33.2 per cent) were not analyzed since they are composed primarily of complex non-hydrocarbons. An overall summary of composition based on a composite of all analyses is presented in Table 18. It is important to emphasize that the mass spectrometer analyses are based on methods developed primarily for petroleum fractions containing substantially low amounts of non-hydrocarbons. In view of the high sulfur and nitrogen content of this oil, these results should be considered only as approximate indications of gross compositional features. This is particularly true in the case of the aromatic fractions, since most of the non-hydrocarbons are concentrated in these fractions.

TABLE 16
Mass Spectrometer Analysis on Non-Aromatic Fraction[a] of Organic Extract from the Challenger Knoll Core

	Weight Per Cent
Paraffins	37.1
1-Ring naphthenes	26.9
2-Ring naphthenes	16.7
3-Ring naphthenes	9.8
4-Ring naphthenes	6.0
5-Ring naphthenes	1.6
6-Ring naphthenes	0.2
Monoaromatics	1.7
Total	100.0

[a] Non-aromatic fraction equals 26.3 weight per cent of sample.

TABLE 17

Approximate Composition by Mass Spectrometry of Aromatic Fractions[a] Separated (GEC) from the Organic Extract of the Challenger Knoll Core

	Initial Aromatic Zone	Mono-Aromatic	Mono and Dinuclear Aromatics	Dinuclear Aromatics	Polynuclear Aromatics	PNA + Soft Resins
Weight Per Cent	3.5	2.6	5.4	8.5	6.7	13.9
			Weight Per Cent			
Alkylbenzenes	26.6	40.5	34.0	10.6[b]	9.2	10.4
Alkylnaphthalenes	33.2	35.0	38.7	17.1	13.6[c]	15.1
Tetralins, indanes, dicyclanobenzenes	9.2	7.4	7.5	21.0	7.8	6.7
Acenaphthenes, biphenyls, fluorenes	5.6	4.1	4.4	16.4	15.6	9.8
Phenanthrenes, anthracenes	4.2	1.2	3.6	15.6	15.7	18.6
Pyrenes	6.7	4.4	4.8	7.9	8.6	11.4
Chrysenes	5.1	3.4	3.1	2.8	5.3	6.8
Benzopyrenes, perylenes	9.5	3.9	4.0	8.7	24.2	21.1
Total	100.1	99.9	100.1	100.1	100.0	99.9

[a] Fractions represent 40.6 per cent of sample
[b] Predominately benzothiophenes
[c] Predominately dibenzothiophenes

TABLE 18
Challenger Knoll Core Organic Extract
Summary of Approximate Composition Determined by Gradient Elution Chromatography and Mass Spectrometry

Sulfur, Weight Per Cent	4.62
Nitrogen, Weight Per Cent	0.28
Paraffins	9.8
1-Ring naphthenes	7.1
2-Ring naphthenes	4.4
3-Ring naphthenes	2.6
4-Ring naphthenes	1.6
5-Ring naphthenes	0.4
Alkylbenzenes	7.2[a]
Alkylnaphthalenes	8.6[b]
Tetralins, indanes, dicyclanobenzenes	4.2
Acenaphthenes, biphenyls, fluorenes	4.3
Phenanthrenes, anthracenes	5.3
Pyrenes	3.4
Chrysenes	2.0
Benzopyrenes, perylenes	5.9
Eluted resins[c]	17.9
Non-eluted asphaltenes + loss[c]	15.3
Total	100.0

[a] Includes benzothiophenes
[b] Includes dibenzothiophenes
[c] Composition undetermined

In general, the composition of this oil does not reveal any unique features that differ greatly from what one experiences with high sulfur petroleum crudes.

Concerning the experimental procedures, details of the gradient elution chromatographic technique have been described previously by Middleton (1967). Basically, the method involves the adsorption of a sample on a short column packed with alumina, followed by the gradual desorption of components in the mixture with solvents of successively increasing polarity. Equal volume fractions are collected with an automatic fraction collector, while the absorbance of the effluent sample-solvent stream is being recorded continuously by an ultra-violet monitor. Sub-fractions are then combined on the basis of gross differences in the absorption curve.

In this particular experiment, 242 milligrams of the stabilized oil was charged to a column packed with 200-mesh alumina (AG-7, Bio-Rad Laboratories). The UV absorption curve obtained is shown in Figure 18.

Mass spectral analyses were performed using the customary techniques for group hydrocarbon analysis. These are based on summations of the ion intensities of selected ions which best characterize the fragmentation (electron impact) modes of the molecular structures either known or suspected to be present in petroleum mixtures. Computing matrices are assembled from averaged data obtained from the mass spectra of both pure hydrocarbons and highly fractionated petroleum concentrates. Tables 19 and 20 list the ion summations used in the analysis of non-aromatic and aromatic fractions, respectively.

The non-aromatic fraction of the oil was analyzed in the above manner using matrix data (32 carbon atom) published by Hood and O'Neal (1959) while the compositions of the aromatic fractions were determined from unpublished matrix data developed at Mobil.

References

Middleton, 1967. *Anl. Chem.* **39**, 1839.

Hood and O'Neal, 1959. **In** *Advances in Mass Spectrometry* (Pergamon Press) 175.

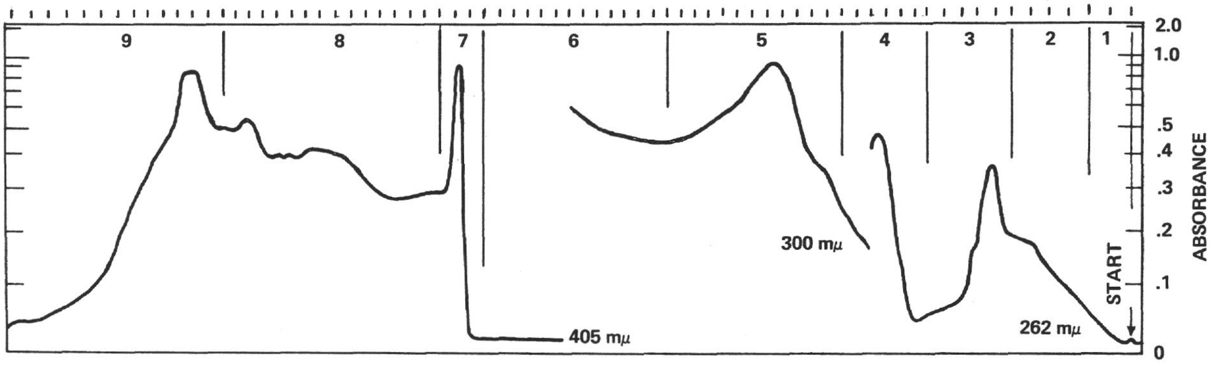

Figure 18. *Gradient elution chromatographic analysis of organic extract from the Challenger Knoll core.*

TABLE 19
Peak Summations Used in "Fragment Ion Matrices" to Determine Composition of Aromatic Hydrocarbon Fractions by Mass Spectrometry

	m/e of Ions in Summation
Alkylbenzenes	$\Sigma\ 77 = 77 + 78 + 91 + 92 + 104 + 105 + 106 + 118 + 119 + 120 + 132 + 133 + 134$
Tetralins, etc.	$\Sigma 117 = 117 + 129 + 130 + 131 + 132 + 143 + 144 + 145 + 146 + 157 + 158 + 159 + 160 + 171 + 172 + 185 + 186 + 199 + 213$
Alkylnaphthalenes	$\Sigma 128 = 128 + 141 + 142 + 154 + 155 + 156 + 168 + 169 + 170 + 182 + 183 + 184$
Acenaphthenes, etc.	$\Sigma 153 = 153 + 154 + 166 + 167 + 168 + 179 + 180 + 181 + 182 + 193 + 194 + 195 + 196 + 209 + 210$
Phenanthrenes, etc.	$\Sigma 177 = 177 + 178 + 191 + 192 + 203 + 204 + 205 + 206 + 217 + 218 + 219 + 220 + 231 + 232$
Pyrenes	$\Sigma 201 = 201 + 202 + 215 + 216 + 229 + 230 + 243 + 244 + 257 + 258 + 271$
Chrysenes	$\Sigma 227 = 227 + 228 + 241 + 242 + 255 + 256 + 269$
Perylenes, etc.	$\Sigma 249 = 249 + 250 + 251 + 252 + 253 + 254 + 263 + 264 + 265 + 266 + 267 + 268 + 277 + 278 + 279 + 280 + 281 + 282$

TABLE 20
Peak Summations Used in "Fragment Ion Matrices" to Determine Composition of Non-Aromatic Hydrocarbon Fractions by Mass Spectrometry

	m/e of Ions in Summation
Paraffins	$\Sigma\ 71 = 71 + 85 + 99 + 113$
1-Ring naphthenes	$\Sigma\ 69 = 69 + 83 + 97 + 111 + 125 + 139$
2-Ring naphthenes	$\Sigma 109 = 109 + 123 + 137 + 151 + 165 + 179 + 193$
3-Ring naphthenes	$\Sigma 149 = 149 + 163 + 177 + 191 + 205 + 219 + 233 + 247$
4-Ring naphthenes	$\Sigma 189 = 189 + 203 + 217 + 231 + 245 + 259 + 273 + 287 + 301$
5-Ring naphthenes	$\Sigma 229 = 229 + 243 + 257 + 271 + 299 + 313 + 327 + 341 + 355$
6-Ring naphthenes	$\Sigma 269 = 269 + 283 + 297 + 311 + 325 + 339 + 353 + 367 + 381 + 395 + 409$
Monoaromatics	$\Sigma\ 91 = 91 + 105 + 117 + 119 + 129 + 131 + 133 + 143 + 145 + 147 + 157 + 159 + 171$

2.12 PORPHYRINS (1.5.2.7)

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Precipitation of asphaltenes from 4.6 grams of Challenger Knoll oil by addition of 15 volumes of petroleum ether gave 0.447 grams of asphaltenes (9.7 per cent of crude). The porphyrin fraction was isolated without demetallation from the asphaltenes by Gel Permeation Chromatography and rechromatography over neutral alumina. Approximately 120×10^{-3} milligrams of vanadyl porphyrin was obtained from 215 milligrams of asphaltene. Experimental methods for isolation and mass spectral analysis have been reported by E. W. Baker and associates (1967).

Vanadyl petroporphyrins were isolated from the Challenger Knoll oil in a yield of about 54 ppm based on the crude oil (*ca.* 560 ppm based on the asphaltenes). The absorption spectrum is typical of vanadyl petroporphyrins with main absorption peaks at 572 (α) and 532 (β) millimicrons (Figure 19). The low α/β peak ratio is indicative of a high ratio of deoxophylloerythroetioporphyrin type (DPEP) to etio type porphyrins. The shoulder at 590 millimicrons has been noted in many other petroporphyrin spectra and is probably due to a small amount (say 10 per cent) of rhodo type porphyrins.

The high DPEP to etio ratio was confirmed by mass spectral analysis which showed major peaks at m/e 583, 569, 555, 541, 527, 513, and 499. The largest peak was at 527 with the other peaks forming a reasonably symmetrical envelope. Peaks of lesser intensity corresponding to the etio series were found at m/e 543, 529, 515, 501 and 487 with 501 being the largest peak in the etio series. The largest peaks correspond to eleven methylene (CH_2) substituents on the porphyrin nucleus in the DPEP series and nine methylene groups in the etio series. Molecular weights extending over the range of several methylene groups are typical of other crude oils of marine origin and the pattern of the envelope is remarkably similar to Belridge crude oil (California, Pliocene) as shown in Figure 20.

Reference

Baker, E. W., Yen, T. F., Rhodes, R. E. and Clark, L. F., 1967. *J. Am. Chem. Soc.* **84**, 3631.

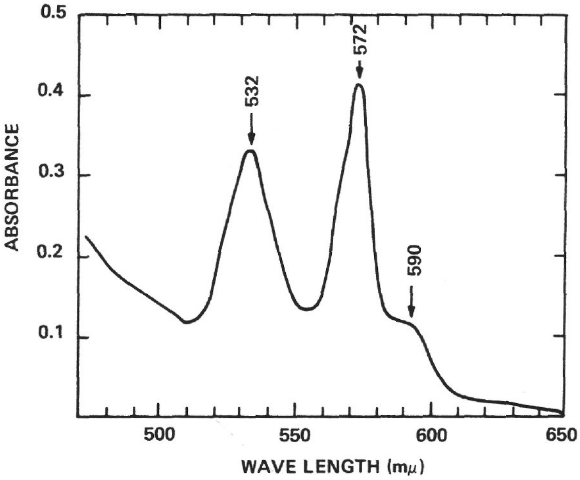

Figure 19. *Spectrum of vanadyl petroporphyrin fraction from Challenger Knoll crude oil.*

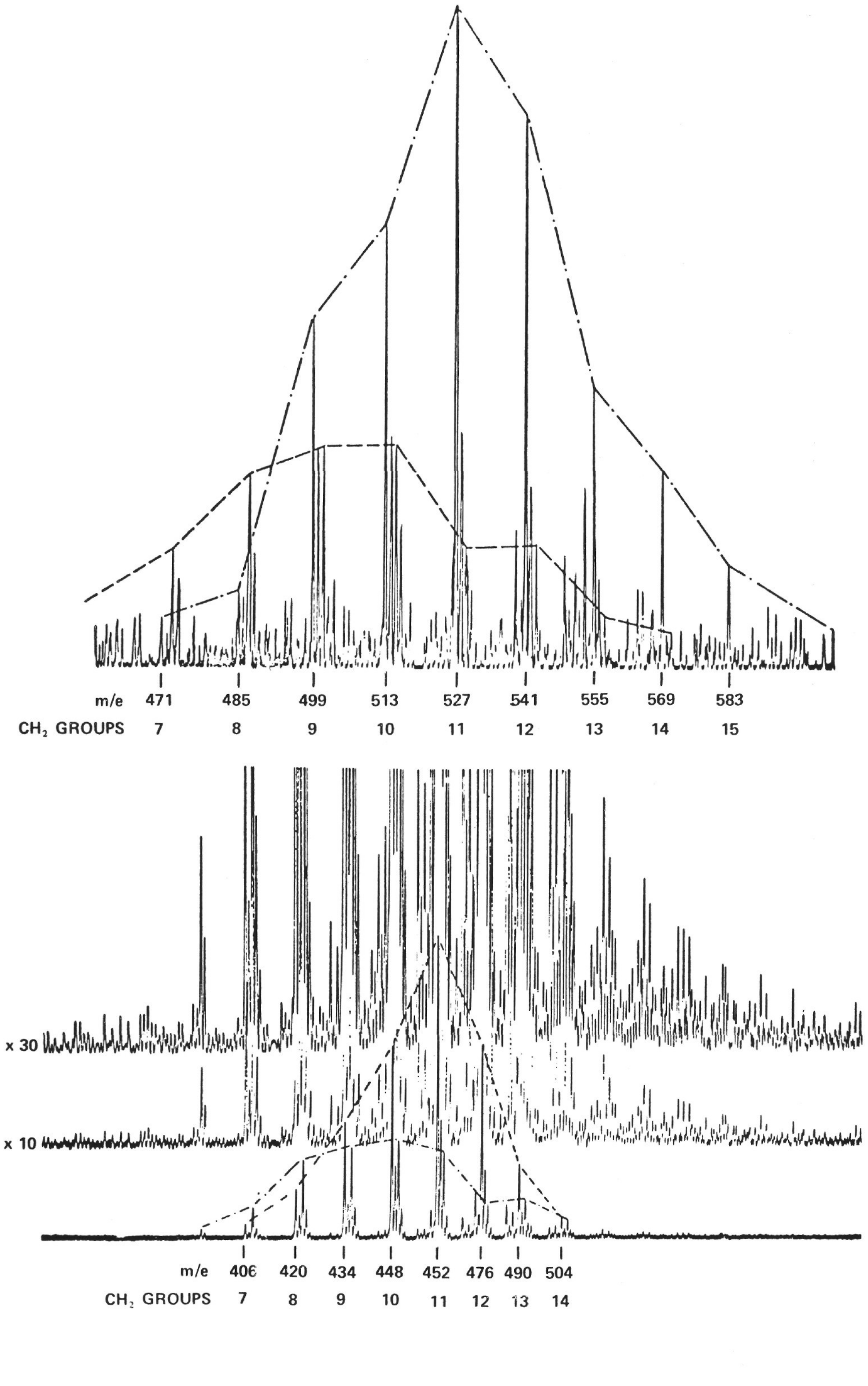

Figure 20. *Mass spectrum analyses of Challenger Knoll and Belridge petroleums.*

2.13 REFERENCE TO C^{13}/C^{12} RATIO OF CHALLENGER KNOLL OIL

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A benzene extract of Challenger (Sigsbee) Knoll Core No. 5 was received for carbon isotope ratio and optical activity measurements. Prior to analysis, the benzene was removed by heating the sample to about 85°C in a stream of nitrogen. After 72 hours of this treatment, infrared spectral analysis indicated that the sample still contained about 1.3 per cent benzene. At this concentration, the C^{13}/C^{12} ratio of the benzene would have to be 10 parts per mil higher or lower than that of the sample to introduce a 0.1 per mil error in analysis, and it was decided to analyze the sample without further treatment. The ratio was found to be +2.6 per mil relative to NBS-22 standard (or -26.8 per mil relative to PDB-1 standard). This value is compared in Figure 21 with carbon isotope ratios of thirty crude oils produced at Louisiana Gulf Coast locations from Miocene reservoirs. It may be worth noting that the isotope ratio of the extract would tend to be slightly higher if its gasoline fraction were not lost.

Satisfactory optical activity runs could not be made on this sample with the equipment available.

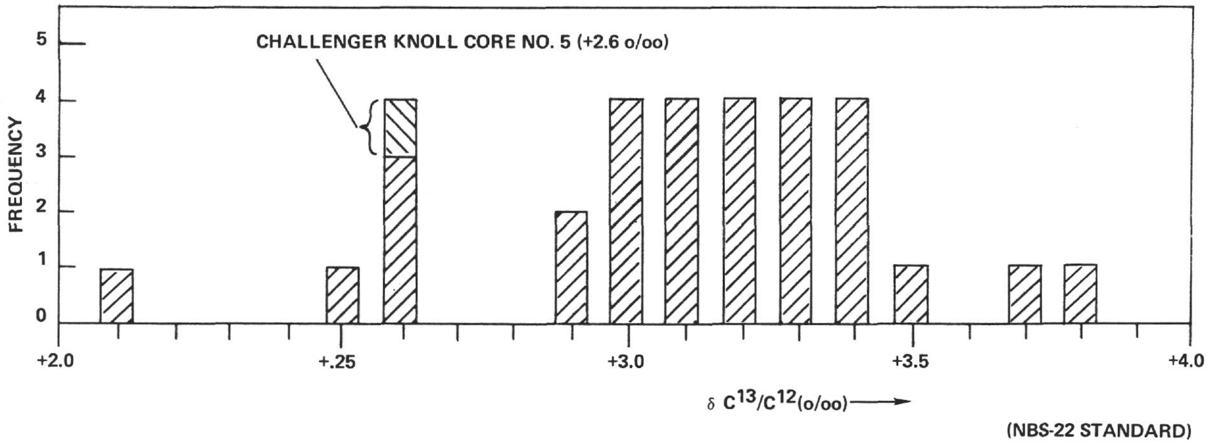

Figure 21. *C^{13}/C^{12} ratio in organic extract from Challenger Knoll (Sigsbee) Core No. 5 and thirty other Gulf Coast crude oils (Miocene).*