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DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR HYDROCARBONS IN MINERAL AGGREGATES

by D. P. Stevenson and A. G. Polgar

Prepared by
SHELL OIL COMPANY
Emeryville, Calif.
for

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ABSTRACT

In this report there are described the results of the assay of the organic chemical constituents, primarily the hydrocarbons, of a variety of terrestrial sediments varying in age from recent ocean bottom sediments to pre-Cambrian slate and samples of five meteorites. Of the group of terrestrial samples examined, ocean bottom cores, shales, slates and limestones, only the last named were found to contain too little hydrocarbon to be detectable. The quantities of organic substances recovered ranged from 10-30 ppm from the very old slates, to 300-800 ppm for the shales and ocean bottom sediments. The lower limits to the organic content of the specimens of the Murray and Hamlet meteorites were found to be 50 and 300 ppm, respectively.

The kinds of hydrocarbon found in the meteorite extracts are very similar in both type and molecular weight distribution to those found in the extracts of the shales and slates. Further the kinds of hydrocarbons and the nature of the molecular weight distribution are such that biochemical processes very likely were required at some stage of their genesis.

One meteoric specimen was found to be contaminated with polychloronaphthalene of the type used as wax extenders and plasticizers during the 1930's.

DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR HYDROCARBONS IN MINERAL AGGREGATES

Introduction

In the previous phase of this investigation, a method was developed, and tested, for the recovery and characterization of small quantities of C_{14} plus, nominally saturated hydrocarbons that may be associated with mineral matter, particularly sedimentary rocks. The method, consisting of Soxhlet extraction of the sample followed by elution chromatography over silica gel and characterization of the isolated fractions by ultraviolet-, infrared- and mass spectrometry, was designed for the purpose of examining the organic chemicals content of meteoritic or other extraterrestrial matter for possible biological origin.

In the present phase of this project, this method, modified in some of its details but also expanded by the incorporation of additional techniques, has been applied to the examination of a variety of meteoritic specimens, and terrestrial rocks spanning a wide geological period. Analytical data on samples in the latter group were to serve as background for the interpretation of results of analyses of the extraterrestrial specimens.

The general scheme of our fractionating procedure is shown in Figure 1. Extraction with n-hexane in a Soxhlet apparatus was always the first step in this procedure; the sample was next extracted with benzene-methanol azeotrope. The extract obtained with n-hexane was then chromatographed on a column of silica gel to produce the saturates (n-hexane eluate), aromatics (benzene eluate), and hetero compounds (benzene-methanol eluate) aggregates of these fractions. Further fractionation of the saturates aggregate by complexing with urea yielded concentrates of normal alkanes (adduct) and of branched-chain and cyclic components (reject). A final purification step through silica gel was needed to isolate some impurities from these last two fractions.

The six final fractions were obtained for every sample that yielded a hexane extract sufficiently large in size to carry it through the complete fractionation procedure. In some instances, however, the urea complexing step, or even the chromatography on silica gel, had to be abandoned due to the lack of minimum sample size needed for these operations.

From some samples, refluxing benzene-methanol azeotrope extracted, in addition to the balance of the organic components, fairly large amounts of inorganic salts as well. Re-extraction with benzene was helpful to produce a fraction free or inorganics from such extracts.

In general, only the end fractions were analyzed. However, the analyses, indicated in brackets under the respective fractions, were all performed only when permitted by the size of these fractions.

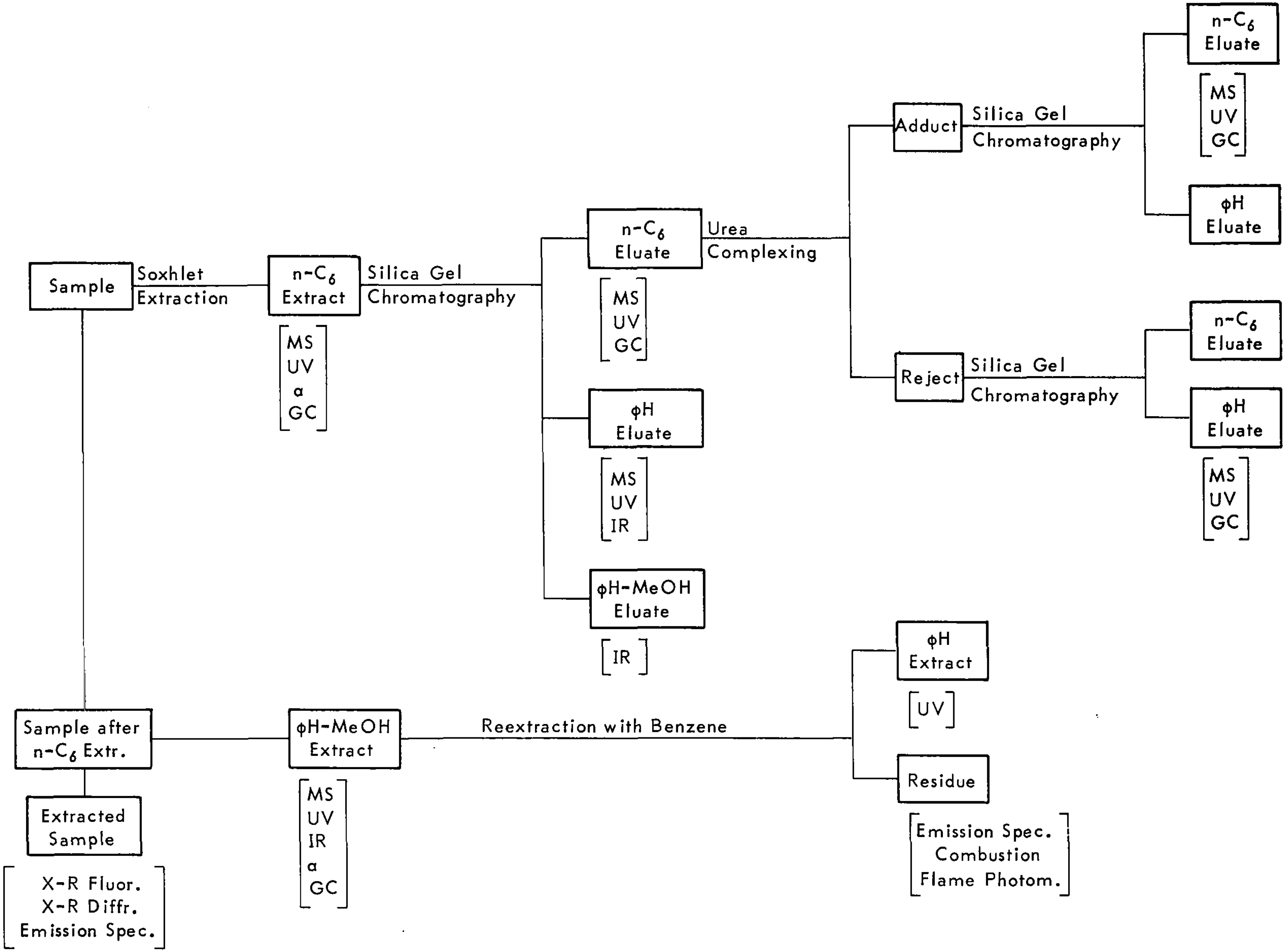

Figure 1. SEPARATION SCHEME

Terrestrial Sedimentary Rock Samples

These samples range from a series of young marine sediments to the nearly three billion-year old pyritic slates from Western Australia (see Table 1). Additional data on these materials are given below.

Ocean Core Segments

Nine ocean core samples were received from Dr. Oliver A. Schaeffer of Department of Chemistry, Brookhaven National Laboratory, who in turn obtained them from M. Ewing of Lamont Geological Observatory. The core itself, designated as No. V18-306, was taken at 07°20' S, 133°03' W, at 4490 meters depth on September 26, 1962. The samples were portions at 35 cm, 1, 2, 3, 4, 5, 6, 7, and 8 m along the core. Most of these samples were moist when received and were, therefore, dried before pulverized. The pulverized samples were light brown in color and ranged from 2 g to 5 g in weight.

Limestones

Three samples were received from the Division of Mines and Geology, State of California, designated as Nos. 1, 3, and 6. One of these specimens came from Mono County, California and was Mississippian in age, the other two were Pennsylvanian in age from San Bernardino County.

Table 1. LIST OF SEDIMENTARY ROCK SAMPLES

Rock Type	Geographical Location	Geological Period	Approx Age, 10^6 yr
Pacific Ocean Sediments (9 samples)	ca 300 mi. north of Darwin, No. Territory, Australia	Pliocene	1 to 8
Coarse-grained "white" limestone	San Bernardino County, California	Pennsylvanian	310
Fine-grained "blue" limestone	San Bernardino County, California	Pennsylvanian	310
"Gray" limestone	Mono County, California	Mississippian	350
Chattanooga Shale	Young's Bend, Tennessee	Upper Devonian	365
Black Shale	Haggum, Sweden	Upper Cambrian	510
Black Shale	Billingen, Sweden	Upper Cambrian	510
Pyritic Slate (2 samples)	Kalgoorlie, Western Australia	Pre-Cambrian	2700

Shales

The three ancient shale samples were received from Lamont Geological Observatory, Columbia University, Palisades, N. Y. Two of these samples are from the Upper Cambrian Black Shale sediments of Southern Sweden whose age is estimated to be greater than 500 million years. One of these specimens is designated as a "Kolm" which indicates an organic-rich pod in a Black Shale sediment. The third sample is somewhat younger in geological age (Upper Devonian, ca 365 million years) and was designated as Chattanooga Shale, Young's Bend, Tennessee, Drill Core YB-9-175.5.

Pyritic Slates

These two specimens of pyritic slates came from Black Flag Sediment in a mine at Kalgoorlie, Western Australia. These sediments have been dated at 2,700 million years of age and are described as pyroclastics and intercalated sediments above a thick sill of quartz dolerite.

The samples we have are:

Specimens	Location	Position in Stratigraphy
WP-26	3820 feet	50 feet above quartz dolerite-Black Flag contact
WP-27	1830 feet	400 feet above quartz dolerite-Black Flag contact

Extraterrestrial Samples

There were six meterоritic specimens on hand for the purpose of this investigation. Three of these were small fragments of the meteorites Orgueil, Murray and Felix, representing the three classes of carbonaceous chondrites (see Table 2). The fourth sample was a fragment of Bruderheim which is classed as a chondrite. These four samples were received from the collection of Professor Melvin Calvin of the University of California, Berkeley. The last two specimens were kindly contributed by Dr. Oliver A. Schaeffer of Brookhaven National Laboratory. The Murray specimen consisted of two larger fragments. Hamlet is considered to be chondritic; the sample was received as a black powder.

To serve as a permanent means of identifying the meteoritic specimens studied in this investigation (Table 2), there were obtained x-ray diffraction (powder) patterns of the specimens. The diffraction patterns are shown in Figures 2 and 3 and the spacings and intensities of the diffraction lines are are given in Table 3. The spacings of the diffraction lines were determined both by measurement with a visual comparitor and from microphotometer tracings from the negatives. Except for a few weak lines and some with large spacings the intensities have been taken from the microphotometer traces. In the case of the Hamlet specimen a diffraction pattern measured with a General Electric Company recording spectrometer was in excellent agreement with the results obtained from photographic records.

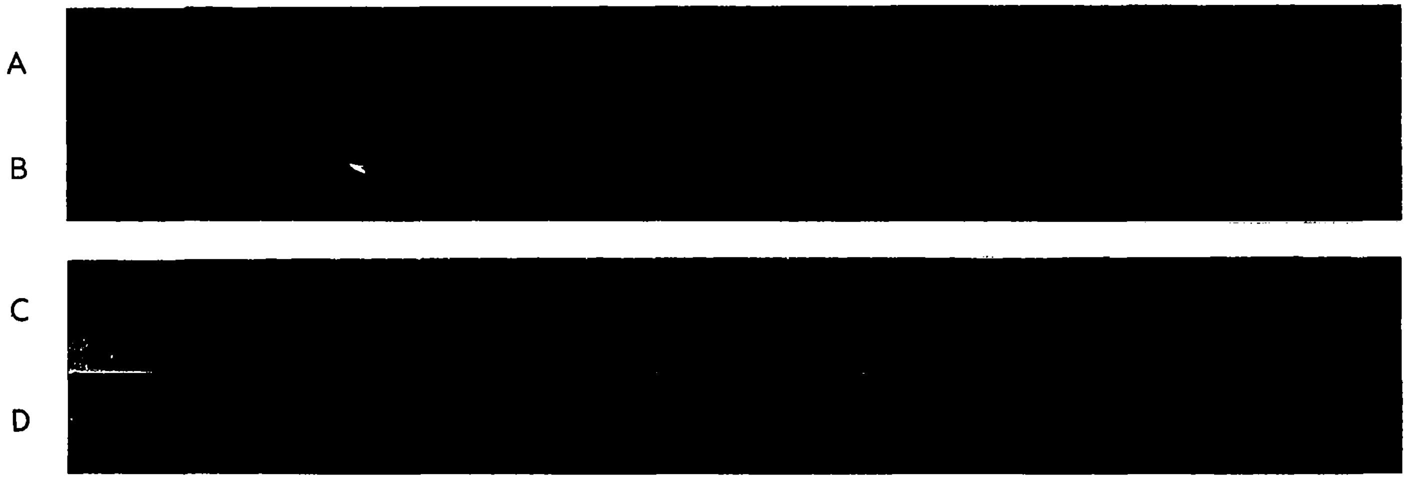

Figure 2. X-RAY DIFFRACTION PATTERNS METEORITIC SPECIMEN EX CALVIN'S LAB
A, Felix: B, Bruderheim: C, Orgueil: D, Murray

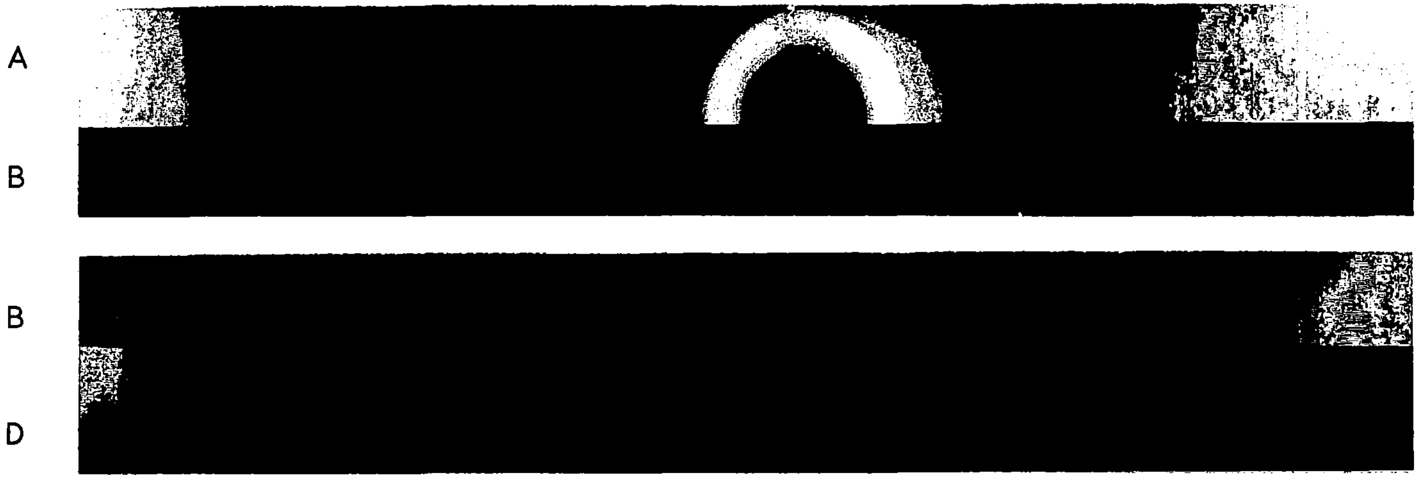

Figure 3. X-RAY DIFFRACTION PATTERNS METEORITIC SPECIMENS EX BROOKHAVEN
A, Ferromagnetic Portion of Murray: B, "Non-Magnetic" Portion of Murray: C, Hamlet

Table 2. METEORITIC SPECIMENS

Name	Group	Location and Date of Fall	Quantity on Hand, g
Orgueil	Type I Carbonaceous Chondrite	Montauban, France May 14, 1864	0.20
Murray	Type II Carbonaceous Chondrite	Calloway County, Kentucky October 20, 1950	0.17
Felix	Type III Carbonaceous Chondrite (olivine-pigeonite)	Perry County, Alabama May 15, 1900	0.25
Bruderheim	Olivine-hypersthene Chondrite	Saskatchewan, Canada, 1960	0.20
Hamlet	Olivine-hypersthene Chondrite	Starke County, Indiana November 13, 1959	1.59
Murray	See above	See above	1.87

Prior to recording the diffraction pattern of the Murray specimen received from Brookhaven, it was divided into two portions with the aid of a magnet - see below. The diffraction patterns of the two portions, nonmagnetic and ferromagnetic were recorded. A very poor pattern was obtained from the ferromagnetic portion, no doubt due to the relatively large size of the particles in this portion of the specimen. Attempts to grind the ferromagnetic portion to smaller particle size in an agate mortar were unsuccessful. Comparison of patterns D of Figure 2 with B of Figure 3 reveals sharper lines in the pattern of the nonmagnetic portion of Murray (from Brookhaven) than the complete Murray from Calvin's Laboratory. The more diffuse pattern in this latter case is probably the result of scattering by the larger particles of the ferromagnetic portion in the unsegregated specimen.

It may be further noted that in the cases of the specimens from Brookhaven the diffraction patterns were recorded after extraction of the constituents with organic liquid solvents. The specimens received from Prof. Calvin were examined as received.

Table 3. X-RAY DIFFRACTION LINES - METEORITIC SPECIMENS

Murray						Felix ex Calvin		Bruderheim ex Calvin		Hamlet ex Brookhaven		Orgueil ex Calvin	
ex Calvin		Nonmagnetic		Magnetic									
d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i
		8.1_3	uf										
7.19	0.07_0									7.1_3	0.14		
				5.8_7	msb					5.9_6	0.025		
										5.3_4	0.04_0		
5.1_5	f	5.12	0.03			5.14	0.04_0	5.09	0.02_5	5.07	0.03_0		
												4.56	0.03_0
						4.26	0.02_0						
		4.02_5	0.02					4.04	0.03_0				
3.89_0	0.06_5	3.88_5	0.08_5	3.8_5	f	3.90_5	0.05_5	3.89_0	0.04_5	3.87_0	0.07		
3.73_5	0.02_0	3.72_7	0.04_5			3.78_7	0.03_0	3.74	0.02_5	3.71_0	0.02_5		
3.59_0	0.03_0									3.55_6	0.06_5		
3.50_0	0.05_0	3.49_0	0.09_5	3.48	m	3.51_0	0.08_5	3.51_0	0.04_0				
3.31	f	3.32	f			3.29	0.01_5	3.32	0.01_5	3.28_0	0.03_5		
3.17_0	0.06_0	3.19_0	0.05_0			3.16_7	0.03_2	3.16_5	0.12	3.16_5	0.07_5		
		3.15_8	0.07_0	3.14_0	0.03_0								
2.98_5	0.09_0	2.99_0	0.10_0			2.98_0	0.07_5	2.97_8	0.06_0	2.97_5	0.07_0	3.00_4	0.04_0
		2.94_0	0.03_0	2.95_0	0.02_0							2.95_4	0.07_0
2.87_3	0.07_0	2.87_5	0.07_5	2.87_2	0.02_0	2.87_2	0.06_5	2.87_8	0.05_0	2.87_0	0.07_0		
				2.82_5	0.01_5	2.79_0	0.14						
2.77_5	0.05_0	2.76_5	0.18	2.77_3	0.03_0			2.78_2	0.05_5	2.76_5	0.03_0		
2.71	vvf							2.70	vvf	2.70_7	0.02_5		
								2.66	uf				
		2.64_0	0.03_0	2.63_3	0.01_9							2.62	0.03
										2.53_2	0.06		
2.51_0	0.14	2.51_5	0.21	2.51_5	0.03_5	2.52_6	0.14	2.52_2	0.14	2.51_0	0.05	2.52_2	0.21

(Continued)

Table 3 (Contd-1). X-RAY DIFFRACTION LINES - METEORITIC SPECIMENS

Murray						Felix ex Calvin		Bruderheim ex Calvin		Hamlet ex Brookhaven		Orgueil ex Calvin	
ex Calvin		Nonmagnetic		Magnetic									
d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i
2.45_4	0.15	2.46_0	0.21	2.46_2	0.05_0	2.47_7	0.18	2.46_9	0.17	2.45_5	0.65_5	2.43	0.03
						2.38	uf						
		2.34_0	0.03_0			2.34	uf						
		2.27_0	0.10_0	2.26_5	0.02_5	2.27_8	0.07_5	2.26_2	0.03_5	2.26_4	0.04		
2.25_8	0.07	2.25_3	0.06_0							2.24_5	0.06		
2.16	uvf	2.16_0	0.04_5	2.17	uuf	2.16_9	0.03_0	2.16_0	0.02_5	2.16_2	0.02_5		
2.12	vvf	2.11_7	0.03_0	2.11_0	0.03			2.10_0	0.05_5	2.11	f		
		2.09_0	0.05_0	2.08_3	0.04_0	2.08_8	0.02_0					2.09_1	0.04_5
				2.06_2	0.03	2.06_3	0.03_0			2.06	vf		
2.02_1	0.04_5	2.03_0	0.04_0	2.02_5	0.04_0	2.02_4	0.12	2.02_0	0.03_0	2.02	uf		
		2.01_7	0.03_0	2.00_0	0.02_0								
		1.96_6	0.03_0					1.96	vvf				
		1.95_0	0.03_0							1.95_5	0.01_5		
						1.82_3	0.03_5						
						1.79_0	0.03_0			1.78_0	0.01_5		
1.74_7	0.08_0	1.75_0	0.14	1.75_3	0.04_5	1.75_8	0.13	1.75_2	0.07_0	1.75_8	0.03_5		
		1.70_0	0.02_0	1.69	vvf					1.69_4	0.02_0	1.70_7	0.03_5
		1.67_2	0.04_0			1.67_5	0.02_5			1.67_2	0.01_5		

(Continued)

Table 3 (Contd-2). X-RAY DIFFRACTION LINES - METEORITIC SPECIMENS

Murray						Felix ex Calvin		Bruderheim ex Calvin		Hemlet ex Brookhaven		Orgueil ex Calvin	
ex Calvin		Nonmagnetic		Magnetic									
d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i	d	log i_0/i
		1.64_0	0.04_0			1.63_3	0.05_0			1.63_5	0.03_0	1.61_2	0.05_0
1.60_5	0.04_0	1.60_2	0.02_0			1.60_3	0.04_0			1.60_5	0.07_0		
1.57	vvf	1.57_5	0.03_0										
				1.55_5	0.02_0							1.56_0	0.02_5
				1.53_6	0.01_5					1.53_2	0.01_5	1.53_0	0.03_5
1.52	vvf	1.52_5	vvf	1.51_3	0.02_0								
1.51	vvf	1.50_5	0.07_0	1.50_0	0.02_0					1.50_2	f		
1.47_5	0.04_0	1.48_5	0.05_0	1.48_7	0.02_0			1.49_0	0.05_5	1.47_2	mf	1.48_0	0.10_5
1.43	vvf	1.44_0	0.02_5										
		1.40_0	0.04_0					1.39_2	0.04_0				
1.37	vvf			1.36	vf			1.35_5	0.03_5				
1.35	vf	1.35_2	0.05_0					1.32_0	0.03_5				
1.32	vvf	1.31_6	0.03_5										
				1.26	vf							1.30_4	0.04_0
												1.27_5	vf
												1.12_0	0.03_0
												1.11_5	0.02_0
												1.09_5	0.04_5

Experimental Techniques

Sample Preparation and Extraction

Samples were prepared for extraction by crushing them in an aluminum bronze mortar, followed by pulverization with a ceramic ball in an alumina-ceramic vial of a high-speed impact shaker. Steel vessels were avoided in all these operations to prevent formation of hydrocarbons which may be produced from carbides of iron in the presence of moisture.

The solvent extraction method described in the Appendix of the Final Report for the period July 1962 to June 1963 has been used for the recovery of organic matter from our terrestrial as well as extraterrestrial samples. However, as an additional safeguard, a slow steam of nitrogen was introduced through the condenser of the Soxhlet apparatus to minimize chances of atmospheric oxidation of the extract. This nitrogen stream, as well as that used in the solvent stripping step, was dried over barium oxide and filtered through cotton and a drop-out canister.

In general, special attention was paid, in all operations, to guard against introducing impurities via reagents, glassware or fall-in from the air. Solvents for extraction were redistilled as described earlier. However, preceding the distillation, n-hexane and benzene were treated with sulfuric acid solutions of appropriate concentrations to remove olefinic impurities which may distill with the major component and could give rise to high-boiling residues by subsequent polymerization. Carbonylic compounds which are possible contaminants in methanol, were removed, prior to distillation, by treatment with dinitrophenylhydrazine. Equipment components were kept under double cover and chances of fall-in from the air were minimized by performing all sample handling within a dust-tight cabinet.

In addition to refluxing in a Soxhlet apparatus, extraction of some of our samples was tried by two other techniques as well.

a) A technique applicable only to carbonate rocks was tested with the limestone specimens. Pulverized sample portions were layered with n-hexane and dissolved in aqueous hydrochloric acid solution. Only a trace of dark powdery residue remained undissolved. After centrifuging, the hydrocarbon layer was siphoned off and evaporated.

b) Some sample portions in n-hexane suspension were exposed to ultrasonic waves (40 Kc) for several 5-minute periods. The decanted solvent portions were centrifuged and evaporated. This technique has been proposed in the literature (R. D. McIver, Geochim. et Cosmochim. Acta <u>26</u>, 343; 1962) to speed up the extraction procedure. With our samples, however, no advantages were apparent.

Fractionation by Adsorption Chromatography

In our Final Report for the period, July 1962 to June 1963, a procedure was described for the small-scale chromatographic fractionation of extracts from mineral aggregates. This method has now been modified in some of its details to satisfy the somewhat different requirements of the present phase of the project. Two column volumes of n-hexane were substituted for isooctane to isolate the saturates portion, followed by two volumes of benzene to desorb the aromatic hydrocarbons content of the sample; nonpolar hetero compounds are known to emerge in this latter fraction. Elution of the column with benzene-methanol azeotrope produced the polar hetero compounds as the balance of the sample.

To prevent contamination of isolated fractions by impurities which may be present in silica gel, the column was prewashed with four volumes of benzene-methanol azeotrope; twenty column volumes of n-hexane were put through this prewashed column prior to charging the sample to displace completely the two polar solvents.

Isolation of Normal Alkanes

It is well known that urea possesses the unique property of forming solid inclusion complexes with straight-chain organic compounds (e.g., L. C. Fetterly, "Organic Adducts", Chapter VIII in "Non-Stoichiometric Compounds", 1963). These complexes have been used to effect separation of n-alkanes, fatty acids, etc., from the isomeric branched-chain compounds. The long chains of these materials are trapped within the helical tunnels of the urea crystal lattice, the ease of formation and the stability of these complexes increasing with increasing chain length. Sample components not acceptable by urea for inclusion may then be extracted by a selective solvent, following which the complexed portion is decomposed with water. The liberated "guest" molecules of the complex are separated by partitioning into a suitable solvent. While this technique has been used successfully to produce high purity normal paraffin fractions from petroleum and its derivatives, it is known that certain branched-chain compounds, or even those containing cyclic structures will form urea complexes provided that there is a sufficiently long straight chain in the molecule and the branch (or cycle) is not too large.

Much attention has been given in recent years to an alternate method for the separation of straight-chain compounds, especially of n-alkanes. Synthetic zeolites with uniform pores close to 5 A in diameter, such as molecular sieve 5A of Linde Air Products Co., have the property of sorbing straight-chain compounds with the exclusion of bulkier branched and cyclic structures thus providing a means for specifically determining n-alkanes in isomeric mixtures. While it has been found that MS-5A does indeed retain all the n-alkanes, it also retains a portion of the isoalkanes and cyclanes present in the experimental samples.[a] This problem is particularly acute when samples in the milligram range are to be fractionated.

Customarily, molecular sieve separations are combined with gas chromatography in a technique that furnishes sample patterns before and after the removal of the n-alkanes portion of the sample. The recovery of the n-alkanes adsorbed in the molecular sieve column is not attempted in this

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a) P. A. Schenck, E. Eisma, Nature 199, 170 (1963).

arrangement. Thus this so-called subtractive gas chromatography is only an analytical scheme that does not permit the subsequent investigation of the n-alkane fraction. The trapped fraction may be recovered quantitatively from the cavities of the molecular sieve only in the lower boiling ranges; desorption of the longer chain alkanes becomes slower and the recovery in the wax range is extremely slow and not quantitative. The loss due to this cause is expected to be higher with decreasing sample sizes.

On the basis of these considerations, extractive crystallization with urea appeared to us as the more suitable technique for producing n-alkanes concentrates from our extracts. The procedure employed consisted of mixing the sample in a light hydrocarbon solution with a methanolic solution of urea (ratio of urea to sample hydrocarbons, approx 10:1), evaporating the solvents, and extracting the dry residue with a light hydrocarbon solvent to obtain the sample portion rejected by the urea. The adduct and the excess urea was then dissolved in water and the complexed portion of the adduct was then decomposed with water and the complexed portion of the sample, representing the aggregate of n-alkanes, partitioned into a light hydrocarbon. Both these fractions were finally chromatographed on silica gel in the micro equipment described earlier to remove small amounts of polar impurities which became associated with these fractions during the urea treatment. Fractions desorbed with n-hexane were ready for further examination.

A petroleum fraction with a carbon number range of C_{16} to C_{30} was used to check this method. The n-alkanes fraction isolated from a 10-mg charge contained only 20-30 percent other hydrocarbons; the over-all recovery was excellent.

Gas Chromatography

Our gas chromatographic equipment was comprised of a Beckman Thermotrac temperature programmer and oven, a Perkin-Elmer sample vaporizer and splitter, and a locally-built flame ionization detector. Golay-type stainless steel open tubular columns with an internal diameter of 0.01 inch were used for most separations because they provide, when combined with programmed temperature control, maximum resolution of complex wide boiling mixtures. Of the different coatings tried, Dow-Corning's DC 710 silicone oil, in a 50-foot column which was programmed at a rate of 3° per minute from 100 to 250°C, was most useful for our purpose.

Polarimetry

A Bendix Automatic Polarimeter, Type 143A, was available to examine sample fractions for optical activity at 5461 A, the wavelength of the filter for which the polarimeter was calibrated. The stability of this instrument was such that rotations could be estimated to ±0.0002° arc. Measurements were made in n-hexane or methanol solutions after the instrument was calibrated for the pure solvents using the same cell assembly.

Fractionation by Means of a Magnet

The pulverized sample was spread in a thin layer near one corner of a sheet of tracing paper streched out horizontally between two clamps. An ALNICO-V horseshoe magnet (325 g) was moved underneath the paper first parallel to the edge of the paper, then continued parallel to the other edge. The material transported to the end of this path was then collected as fraction M. The remainder of the sample was designated as fraction NM.

The two meteoritic samples from the Brookhaven National Laboratory, both extracted previously, were treated by this technique. The Murray sample yielded a 12 percent M fraction; however, the Hamlet sample was transportable in toto.

Fractionation and Analysis of Ocean Core Segments

The core samples were first extracted with n-hexane in the Soxhlet apparatus using medium porosity alundum thimbles. No extract was obtained from core sections below 2 meters; the residues from the 35-cm, 1-m, and 2-m samples weighed 1.0, 0.4 and 0.7 mg, respectively (see Table 4).

Table 4. EXTRACTION OF OCEAN CORE SEGMENTS

Abbreviations in parentheses show analyses performed:
M = mass spectrum
U = ultraviolet spectrum
I = infrared spectrum
G = gas chromatogram

Segment	Sample Weight, g	Hexane Extract, mg	Benzene-Methanol Extract Re-extracted	
			Benzene Extract, mg	Residue, mg
35 cm	5.14	1.0 (M)	0 –	–
1 m	1.98	0.4 (M)	0.1 (U)	23.3
2 m	2.81	0.7 (MU)	1.0 (U)	190. (I)
3 m	2.22	0.1 (M)	0.3 (U)	113.
4 m	3.02	0.0	–	–

The low level of hexane extractables in the core samples suggested that their contents of organic material may be nonhydrocarbons (hetero compounds) which, due to the relatively young geological age of these sediments, or because of the lack of catalytic or microbial action, have not been reduced to any significant extent to render them soluble in a saturated hydrocarbon. However, when the extraction of these segments was repeated with the azeotropic mixture of benzene-methanol, the appearance of the residues strongly suggested that they are mainly inorganic in composition. Re-extraction with hot benzene yielded yellowish, oil fractions which weighed less than a milligram.

The still slightly yellow residues of these re-extractions were soluble in water. The one originating from the 1-m core section was examined further. Cathode Layer Emission Spectrography showed its metals content to be mainly Na (95%), with 1 to 3% Si, B and Mo, and traces of Mg, Fe, Al, V, Cr and Ca. The presence of chloride ion was evidenced by a heavy precipitate with silver nitrate solution. A 10.0% carbon content was, however, the indication of some residual organic content.

The meager yields of organic extractables from these samples was an obvious disappointment to us; however, the geographic location of the collection site offers a rational explanation for the near absence of organics. Normal decay to CO_2 and H_2O of plant material in surface deposits is quite rapid if not covered by sediment. This so-called "short cycle or organic matter" exists also in sea water and should be the more pronounced the farther the location is from the influx of sediment carrying rivers. Underwater currents, depth and absorbed oxygen are other factors which affect the level of organic matter in ocean waters and, consequently, the extent and nature of carbonaceous deposits on the bottom.

The core that furnished our sediment samples was taken at a considerable depth (4490 meters) and several hundred miles from the nearest river delta. Since sedimentation at such a location should be slow, very little settled plant (or animal) matter may be expected to survive as distinct organic compounds.

As is indicated in Table 4, mass spectra were recorded of the hexane extracts of the cores from 0.35, 1.00, 2.00 and 3.00 m. The only significant differences between the spectra of the four extracts that are apparent in qualitative comparison are the difference in total intensity of ions and the range in molecular weight of ions; both of these differences in the mass spectra are attributable to the quantity of material it was possible to introduce to the mass spectrometer reservoir. Because of the low intensity of ion currents in the mass spectra of the 1-m and 3-m extracts, only the spectra of the 0.35-m and 2.00-m cores were examined quantitatively.

From the precise mass-to-charge ratios of the ions measured in the high resolution mass spectrometer it was found that essentially three classes of substance could be identified. These are hydrocarbons with empirical formulae:

$$C_nH_{2n+j} \text{ with } -10 \leq j \leq 2 \quad (j \text{ even})$$

$$8 \leq n \leq 42$$

and

$$C_mH_{2m+k} \text{ with } -24 \leq k \leq -12 \quad (k \text{ even})$$

$$10 \leq m \leq 35.$$

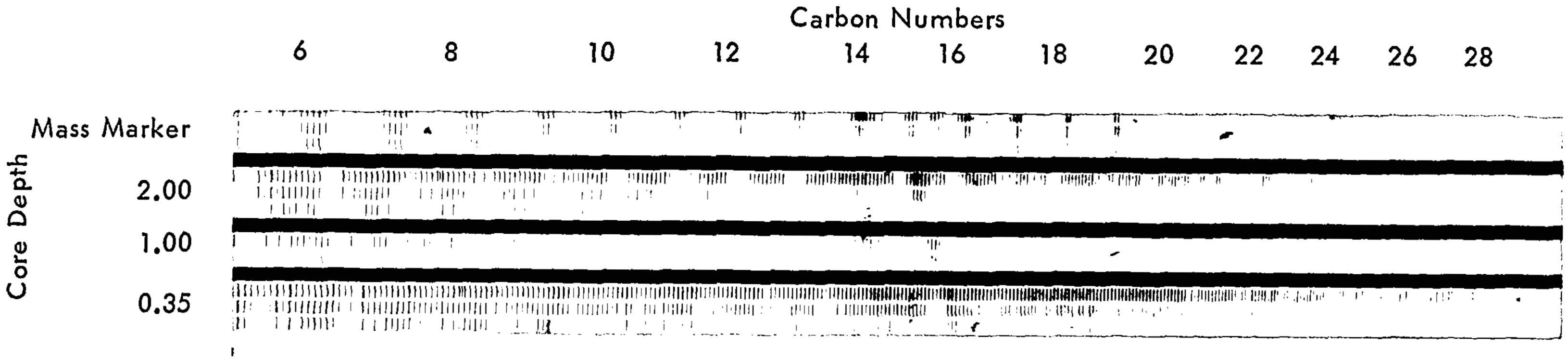

Figure 4. MASS SPECTRA OF OCEAN CORE EXTRACTS. Top three spectra those of a C_{14}-C_{19} normal alkane mixture to provide near scale. The much weaker spectrum of the 1.0m extract is due to smaller sample.

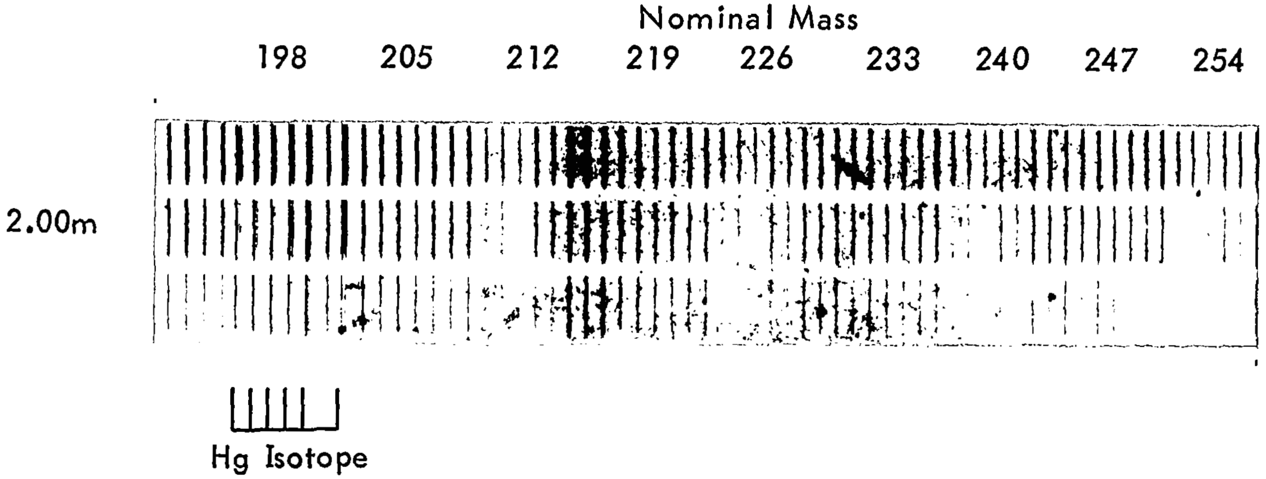

Figure 5. ENLARGEMENT OF A PORTION OF THE MASS SPECTRUM OF THE EXTRACT FROM THE 2.00m OCEAN CORE. (SEE FIGURE 4)
Note that virtually all "lines" are doublets corresponding to the numerical isosteres, $C_nH_m^+$ and $C_{n+1}H_{m-12}^+$

Further, there were found considerably lower concentrations of oxygen-containing compounds. The ions of the mass spectra of the oxygen-containing compounds were virtually all representable by the empirical formulae:

$$C_\ell H_{2\ell+i}O \qquad -10 \leq i \leq 2 \quad (\ell \text{ even and odd})$$

$$2 \leq \ell \leq 10.$$

From the intensities of the ions of the three classes of substance we estimate the distribution to be:

	Volume, %	
	0.35 m	2.00 m
Saturated plus monoaromatic hydrocarbons	90-84	96-92
Polynuclear aromatic hydrocarbons	8-12	4- 6
Oxygenates	2- 4	1- 2

As calculated by a modified parent peak method, the distribution in empirical formulae of the hydrocarbons in the hexane extracts of the 0.35 and 2.00-m ocean cores are found to be those shown in Table 5. It may be seen in this table that there are no significant differences between the hydrocarbon distributions in these two core samples.

Table 5. DISTRIBUTION OF OCEAN CORE HYDROCARBONS IN EMPIRICAL FORMULAE FROM CARBON NUMBER ≥ 14

Hydrocarbons	%v	
	0.35 m	2.00 m
Saturated + Monoaromatic		
C_nH_{2n+2}	21.5	20.0
C_nH_{2n}	24.5	26.2
C_nH_{2n-2}	20.3	21.2
C_nH_{2n-4}	12.7	13.5
C_nH_{2n-6}	11.2	10.4
C_nH_{2n-8}	6.8	6.2
C_nH_{2n-10}	3.0	2.5
	100.	100.
Polyaromatic		
C_nH_{2n-12}	28.2	32.2
C_nH_{2n-14}	19.7	20.9
C_nH_{2n-16}	16.3	16.3
C_nH_{2n-18}	15.0	11.6
C_nH_{2n-20}	9.5	10.8
C_nH_{2n-22}	6.7	7.4
C_nH_{2n-24}	4.5	0.8
	100.	100.

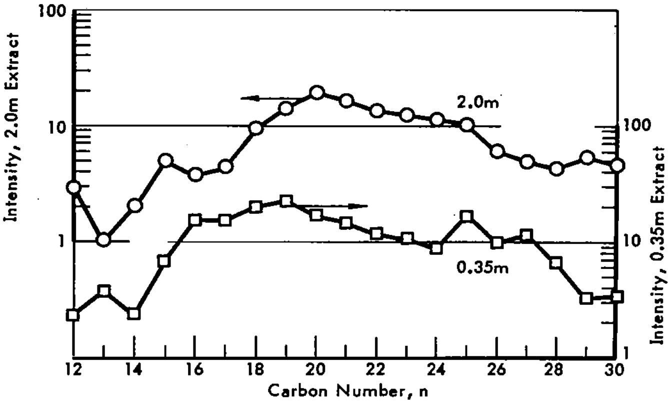

Figure 6. ALKANE ($C_nH_{2n+2}^+$) IONS IN THE MASS SPECTRA OF OCEAN CORE, HEXANE EXTRACTS

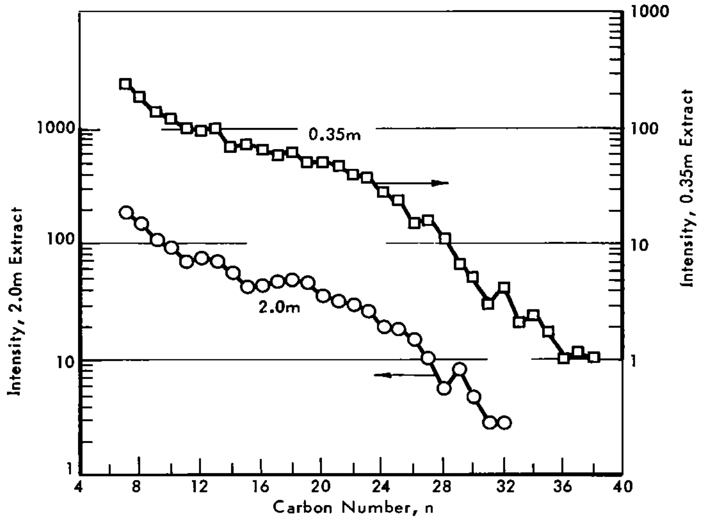

Figure 7. ALKYL ($C_nH_{2n+1}^+$) IONS OF THE MASS SPECTRA OF OCEAN CORE, HEXANE EXTRACTS

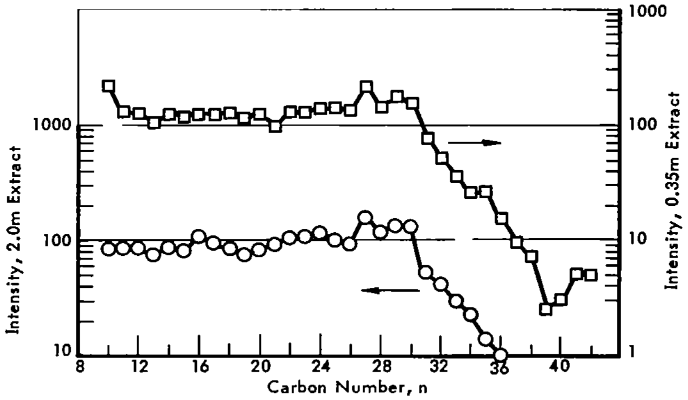

Figure 8. IONS, $C_nH_{2n-6}^+$, OF THE MASS SPECTRA OF OCEAN CORE, HEXANE EXTRACTS

There are shown in Figures 6, 7 and 8 the distribution of mass spectral intensity in carbon number of the ions, $C_nH_{2n+2}^+$ (alkane ions), $C_nH_{2n+1}^+$ (alkyl ions) and $C_nH_{2n-8}^+$ (tetracyclane and alkyl benzene ions) respectively of the hexane extracts of the 0.35- and 2.00-m ocean core specimens. We see in these data some differences between the organic composition of the two specimens. In the case of the alkanes, the extract from the 0.35-m specimen is trimodal with intensity maxima at carbon number, n, equal to 19, 25, and 27, whereas the extract from the 2.00-m specimen has a bimodal intensity distribution with maxima at n = 20 and 29.

The alkyl ion distribution in carbon number is diagnostic of the structure of the alkanes. For a purely normal alkane mixture, intensity of ions should fall continuously with increasing carbon number. The deviation from a smooth decrease in intensity with increasing carbon number indicates these to be in the case of the hexane extracts from both core specimens branched alkanes with defined structure. In particular the intensity maximum found at n = 13 is rather definite evidence of the presence of alkanes of the so-called isoprenoid structure, i.e., 2,6,10-polymethyl alkanes.

The distribution in intensity of the $C_nH_{2n-8}^+$ ions in the mass spectra of the hexane extracts of the 0.35- and 2.00-m ocean cores are quite indistinguished but for the marked excess intensity for carbon number, n = 27, 28, 29 and 30. This behavior is similar to that found in the saturated hydrocarbons from asphaltic or naphthenic petroleums where it has been found that the greater the excess intensity of C_nH_{2n-8} ion at n = 27, 28, 29 and 30, the greater is the optical rotary power of the oil. A perhydrocyclopentanophenanthrene structure has been usually attributed to these substances in petroleum.

Fractionation of Limestones

Samples were crushed, pulverized and extracted in the Soxhlet apparatus with n-hexane. Residues from these experiments, as well as from extractions with ultrasonic waves, or after dissolution with hydrochloric acid, according to procedures described earlier in this report, were extremely small, corresponding to between 1 and 4 ppm extractables. In view of these low yields, no further work was attempted on these materials.

Fractionation of Shales, Pyritic Slates and Meteorites

Shales

All three shale samples were crushed, pulverized, and carried through the full fractionation scheme shown in Figure 1. Yields are given in Table 6. It will be noted that in addition to the standard silica gel column, a mixed bed column was also used to chromatograph a second portion of the hexane extract of the Chattanooga shale sample. A small bed of activated alumina was packed to the top of the silica gel column to improve the separation between the saturates and aromatics of this sample that was found to be unsatisfactory by silica gel alone. The fact that separation with the mixed-bed column was even less satisfactory than with the standard column points to some peculiarities in the molecular composition of the Chattanooga shale extract.

Table 6. FRACTIONATION OF THE SHALE SAMPLES

Abbreviations in parentheses show analyses performed:
M = mass spectrum
U = ultraviolet spectrum
I = infrared spectrum
G = gas chromatogram

Fraction	Weight of Fraction, mg			
	Upper Cambrian Black Shale	Kolm From Upper Cambrian Black Shale	Chattanooga Shale	
Sample	18,400	11,330	20,800	
Soxhlet Extraction				
Hexane extract	12.9 (MG)	6.4 (MG)	29.8 (MG)	
Benzene-methanol extract	29.1 (G)	172.7 (G)	37.3 (G)	
Chromatography of the Hexane Extract			(a)	(b)
Hexane eluate	1.3	3.1	2.0	8.0
Benzene eluate	2.9 (U)	0.9 (U)	3.6 (U)	1.1 (U)
Benzene-methanol eluate	0.4 (I)	0.8 (I)	0.6 (I)	0.8 (I)
Urea Complexing of the Hexane Eluate			(c)	
Adduct	0.3 (MG)	0.7 (MG)	0.6 (MG)	
Reject	0.8 (MG)	1.5 (MG)	3.5 (MG)	

a) Micro column packed with silica gel; one-third of the hexane extract charged.
b) A small bed of alumina packed on top of the silica gel; two-thirds of the hexane extract charged.
c) The two hexane eluates were combined.

The hexane extracts from all three shales were oils and light yellow in color. The final saturates fractions were colorless and, at least in part, crystalline. In contrast, all benzene-methanol extracts, as well as the benzene and benzene-methanol eluates of the chromatographic fractions, were mainly dark brown solids, mixed only in a few cases with dark, oily droplets.

Pyritic Slates

The approximately 5-cm core sections of the two Kalgoorlie slate samples were crushed, pulverized, the fractionated according to the scheme shown in Figure 1. Yields are given in Table 7. The two hexane fractions obtained in the hexane extractions were both bright lemon-yellow in color and partly crystalline. The benzene methanol extract of WP-27 was also light yellow; the corresponding extract from WP-26, however, as well as the other fractions obtained in the subsequent separation steps were similar in appearance to those of the shales series (see previous section).

Table 7. FRACTIONATION OF THE PYRITIC SLATES

Abbreviations in parentheses show analyses performed:
M = mass spectrum
U = ultraviolet spectrum
I = infrared spectrum
G = gas chromatogram

Fraction	Weight of Fraction, mg	
	Kalgoorlie Slate WP-26	Kalgoorlie Slate WP-27
Sample	199,780	133,920
Soxhlet Extraction		
Hexane extract	32.3 (G)	14.0 (G)
Benzene-methanol extract	40.7 (G)	102.0 (G)
Chromatography of the Hexane Extract		
Hexane eluate	2.0	3.3
Benzene eluate	0.2 (U)	0.3 (U)
Benzene-methanol eluate	0.3 (I)	0.2 (I)
Urea Complexing of the Hexane Eluate		
Adduct	0.4 (MG)	1.0 (MG)
Reject	0.9 (MG)	1.3 (MG)

The unusually large benzene-methanol extract of WP-27 was suspected, as similar extracts of most other samples, to be mainly inorganic in composition. Elemental analysis by a variety of techniques confirmed this assumption, as shown in Table 8.

Table 8. ELEMENTAL COMPOSITION OF THE BENZENE - METHANOL EXTRACT FROM KALGOORLIE SLATE WP-27

Element	Percent by Weight	Method
Carbon	0.9	Combustion
Hydrogen	2.1	
Sulfur	1.1	
Chlorine	43.3	
Nitrogen	0.1	
Silicon	9.	Emission Spectroscopy
Magnesium	5.	
Aluminum	0.24	
Vanadium	0.03	
Copper	0.11	
Manganese	0.08	
Chromium	<0.01	
Calcium	0.9	
Barium	<0.01	
Sodium	17.	Flame Photometry
Phosphorus	<6 ppm	Colorimetry
Total	80	

Meteorites

Of the six meteoritic materials, only the Hamlet and the larger Murray samples were considered sufficiently large for extraction (see Table 9). The Hamlet sample was received as a powder, but the two granules of Murray needed grinding. The hexane extract of Murray was entirely too small for further fractionation. The Hamlet sample yielded larger extracts which, however, were suspected of being largely inorganic. This proved to be the case for the hexane extract when a total of less than one-half milligram was recovered in the three fractions of the chromatographic separation.

The residues of the Hamlet hexane extract, as well as those of its two chromatographic eluates, were colorless and the two latter ones in part crystalline. The hexane extract from the Murray sample was also colorless and oily. The benzene-methanol residues, on the other hand, were both colored and did not appear to be homogeneous.

The hexane extract of Hamlet, and the benzene-methanol extracts of both the Murray and Hamlet were checked for optical activity. Neither of the two benzene-methanol fractions showed any rotation. The slight leavo-rotation of the hexane extract of Hamlet, -0.0002° (c = 5.6 mg/5 ml hexane), was on the limit of readability for the instrument, and may be judged inconclusive.

Table 9. FRACTIONATION OF TWO METEORITIC SAMPLES

Abbreviations in parentheses show analyses performed:

M = mass spectrum
U = ultraviolet spectrum
I = infrared spectrum
G = gas chromatogram

Fraction	Wt of Fraction, mg	
	Murray	Hamlet
Sample	1,803	1,589
Soxhlet Extraction		
Hexane extract	0.1 (M)	5.6
Benzene-methanol extract	0.9 (M)	7.3 (M)
Chromatography of the Hexane Extract		
Hexane eluate	-	0.2 (MG)
Benzene eluate	-	0.2 (U)
Benzene-methanol eluate	-	0.05

Mass Spectrometry of Shale and Slate Extracts

As is shown in Tables 6 and 7 the quantity of hexane extract from the three shale and two slate specimens was sufficiently large in each case to permit chromatographic separation of a saturated hydrocarbon fraction and to further subdivide this saturate from action into urea adduct and urea reject fractions. High resolution mass spectra were obtained of each of these ten saturated hydrocarbon aggregates, and application of the modified parent peak method to these mass spectra leads to the distribution in empirical formulae shown in Table 10, for the carbon number, $n \geq 14$, hydrocarbons. In Table 11 there are given the composition of the hexane eluates from the chromatographic separation of the hexane (Soxhlet) extracts of the shales and slates calculated from the data of Table 10, and the relative quantities of urea adduct and reject shown in Table 6 and 7. These "reconstituted" compositions are shown for later comparison with data on the Murray and Hamlet meteorite extracts.

Table 10. DISTRIBUTION IN EMPIRICAL FORMULA, C_nH_{2n+j} $(-10 \leq j \leq +2)$ OF SATURATED HYDROCARBONS EX SHALES AND SLATES

Hydrocarbons	%v				
	Shales			Slates	
	U.C. B.S.	Kolm	Chat.	WP-26	WP-27
Urea Complexes (Adducts)					
C_nH_{2n+2}	52.6	47.9	68.4	58.7	73.3
C_nH_{2n}	19.1	20.1	15.1	14.9	12.0
C_nH_{2n-2}	12.4	14.2	7.3	10.2	6.7
C_nH_{2n-4}	6.5	7.8	3.9	5.6	3.6
C_nH_{2n-6}	5.2	5.4	2.9	4.8	2.5
C_nH_{2n-8}	2.7	2.9	1.6	3.0	1.3
C_nH_{2n-10}	1.5	1.8	0.9	2.8	0.7
Urea Rejects					
C_nH_{2n+2}	18.6	26.5	26.6	17.9	21.4
C_nH_{2n}	21.6	27.1	29.9	25.8	29.5
C_nH_{2n-2}	17.8	20.8	19.3	22.8	21.5
C_nH_{2n-4}	12.3	11.5	10.4	13.8	12.7
C_nH_{2n-6}	15.1	7.7	7.9	11.7	9.3
C_nH_{2n-8}	9.3	4.1	4.1	5.5	4.0
C_nH_{2n-10}	5.4	2.3	2.0	2.5	1.5

In Table 11 there are also shown the results of similar analyses of similar extracts of an upper cretaceous sandy shale, a Mississippi-Pennsylvania limestone and a Silurian-Niagran limestone.a)

It may be seen that there is no correlation between the composition of the hydrocarbons found in a sedimentary rock, as measured in terms of the parent peak determination of distribution in empirical formula, and either the age of the rock or its character, limestone, shale or slate.

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a) Contract No. NASw-438, Final Report, July 1962-June 1963.

Table 11. DISTRIBUTION IN EMPIRICAL FORMULAE OF THE TOTAL SATURATES IN THE HEXANE EXTRACTS OF SHALES AND SLATES

Hydrocarbons	%v					Sandy Shale	M-P Limestone	S-N Limestone
	Shales			Slates				
	U.C. B.S.	Kolm	Chat.	WP-26	WP-27			
C_nH_{2n+2}	27.9	33.3	32.7	30.5	44.1	20.7	36.3	24.4
C_nH_{2n}	20.9	24.9	27.7	22.5	21.9	33.0	29.7	34.0
C_nH_{2n-2}	16.3	18.7	17.5	18.9	15.1	12.0	14.6	20.1
C_nH_{2n-4}	10.7	10.3	9.5	11.3	8.8	12.0	8.0	11.0
C_nH_{2n-6}	11.6	7.0	7.1	9.6	6.4	6.8	7.9	6.7
C_nH_{2n-8}	7.5	3.7	3.7	4.8	2.9	3.1	2.7	2.7
C_nH_{2n-10}	4.3	2.2	1.8	2.6	1.2	1.3	0.8	1.2
Age, 10^6 yr	≥ 500	≥ 500	~360	2,700	2,700	90 ± 20	~310	~420

In Figures 9, 10, 11, 12, 13 and 14 there are compared the distribution of intensity in carbon number of the ions $C_nH_{2n+2}^+$ of the urea adducts and rejects of the three shale and two slate specimens. We find that in all cases the average carbon number of the alkanes in the urea adduct to be greater than that of the corresponding urea reject. In the cases of the urea adducts from the upper Cambrian Black Shale and Kolm and one of the slates (WP-26), the alkanes show a very well defined bimodal distribution with intensity maxima for $n = 17$ to 19 and 23-25. Similar bimodal distribution of alkane ions in carbon number were previously found in the hexane extracts for the Mississippi-Pennsylvania and Silurian-Niagran limestones but not in the Upper Cretaceous Sandy Shale (Shale A of previous report).

In all five cases the distribution of intensity of the $C_nH_{2n+2}^+$ ions in carbon number in the mass spectra of the urea rejects can be best described as irregular or polymodal.

Whereas the distribution of intensity of $C_nH_{2n+2}^+$ ions in carbon number $\underline{n}$ provides a picture of the distribution of alkanes in the sample in molecular weight, the distribution of intensity of $C_nH_{2n+1}^+$ ions in carbon number gives an indication of the structure of the alkanes. In Figures 15 and 16 there are shown the intensity of $C_nH_{2n+1}^+$ ions vs n for the various shale and slate extract saturates along with those of three normal alkane control mixtures. The distribution of the normal alkanes in molecular weight in the controls is shown in Figure 9 above.

It may be seen in curves I of Figure 15 and III and IV of Figure 16 that mixtures of normal alkanes give distributions of $C_nH_{2n+1}^+$ intensity in n

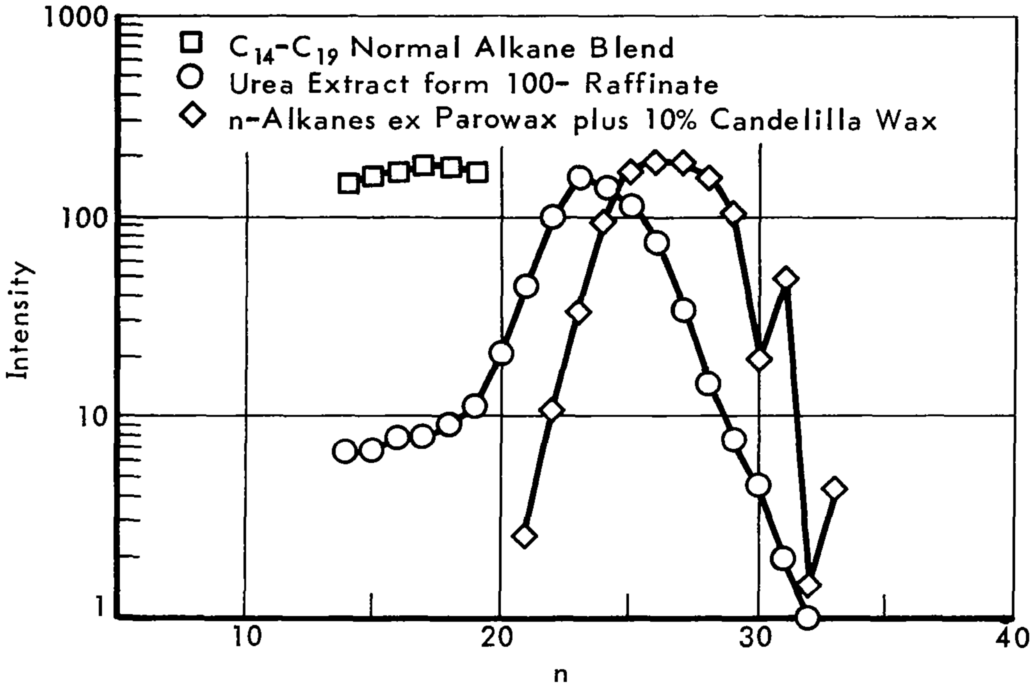

Figure 9. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTIONS IN, n, FOR MASS SPECTROMETER CONTROL MIXTURES

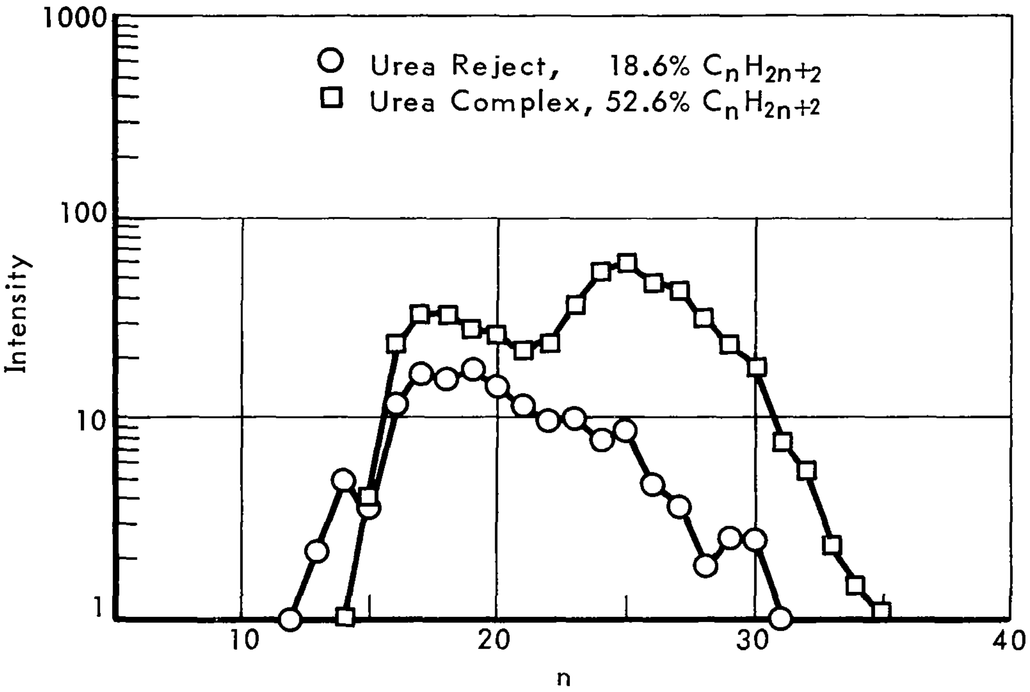

Figure 10. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT AND REJECT FRACTIONS OF BLACK SHALE

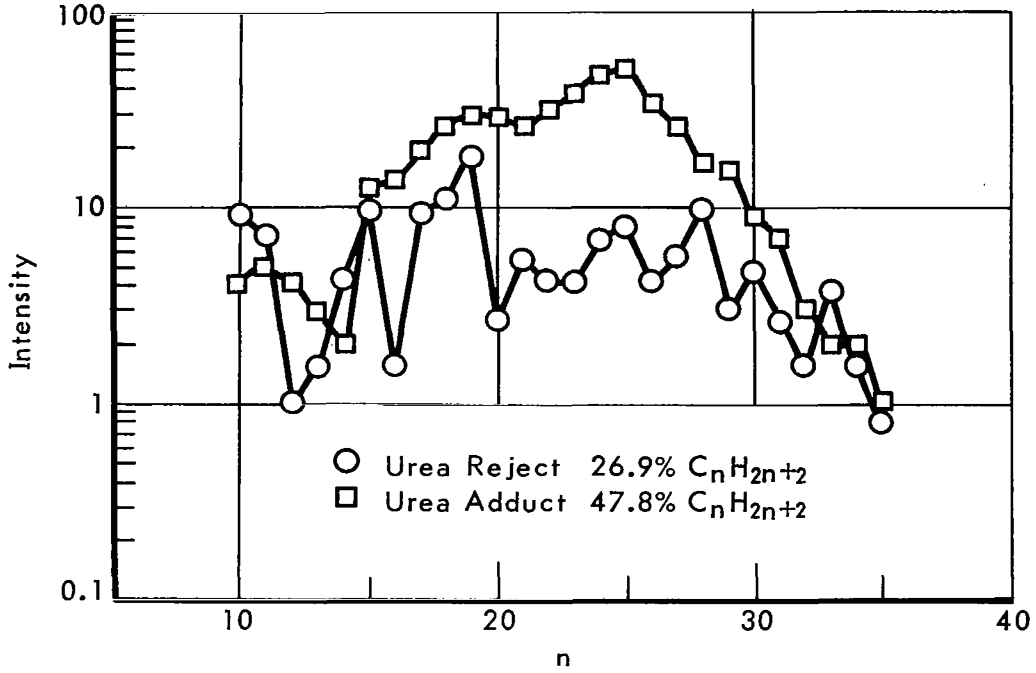

Figure 11. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT AND REJECT FRACTIONS OF BLACK SHALE KOLM

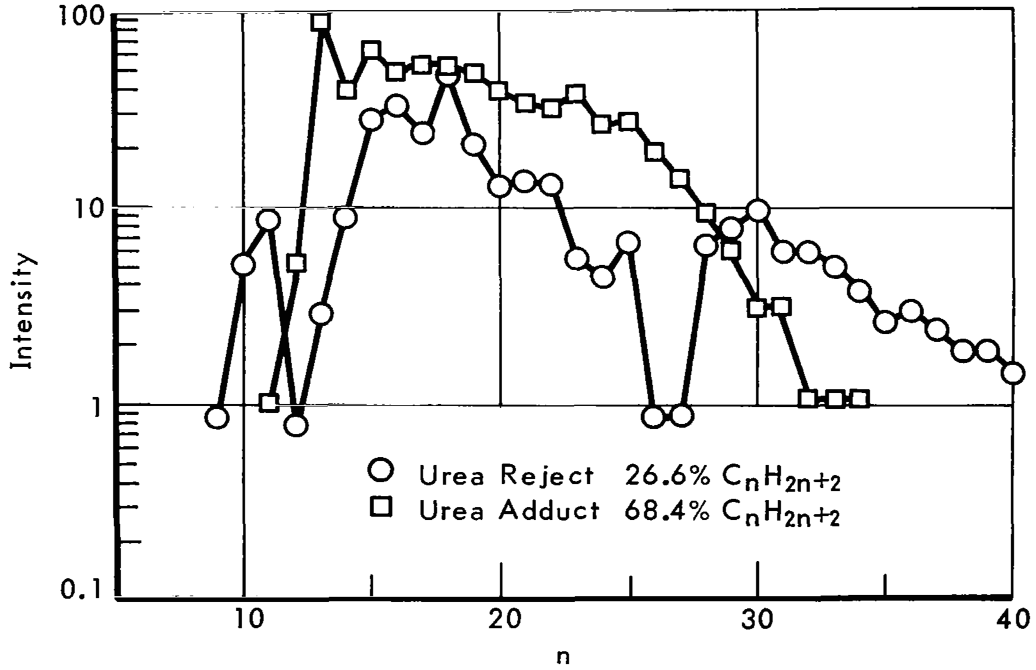

Figure 12. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT AND REJECT FRACTIONS OF CHATTANOOGA SHALE

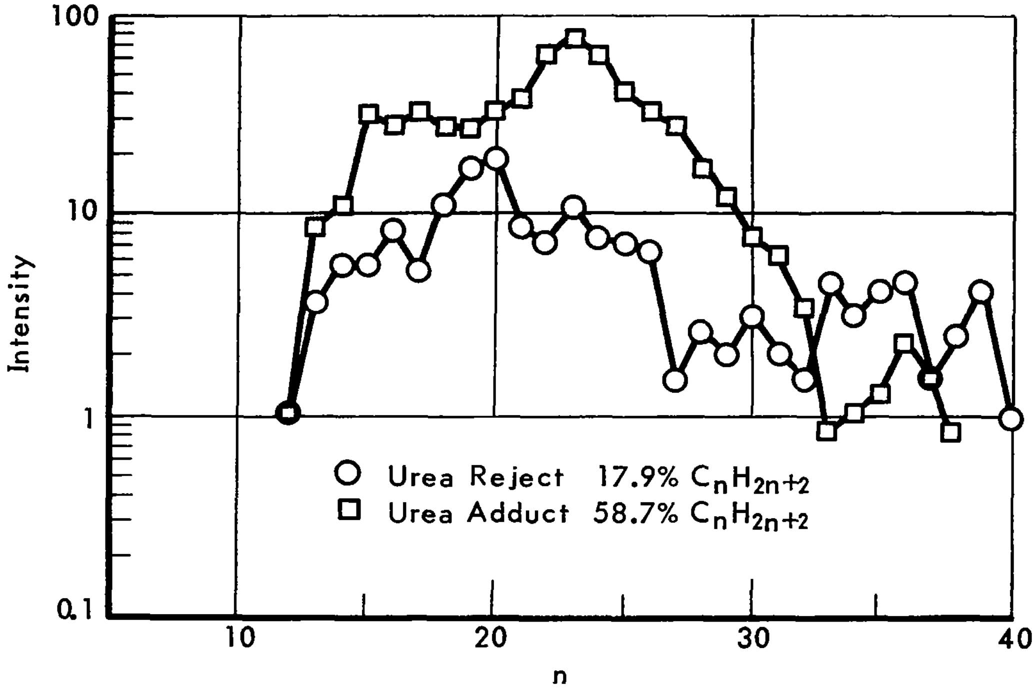

Figure 13. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT AND REJECT FRACTIONS OF KALGOORLIE SLATE WP-26

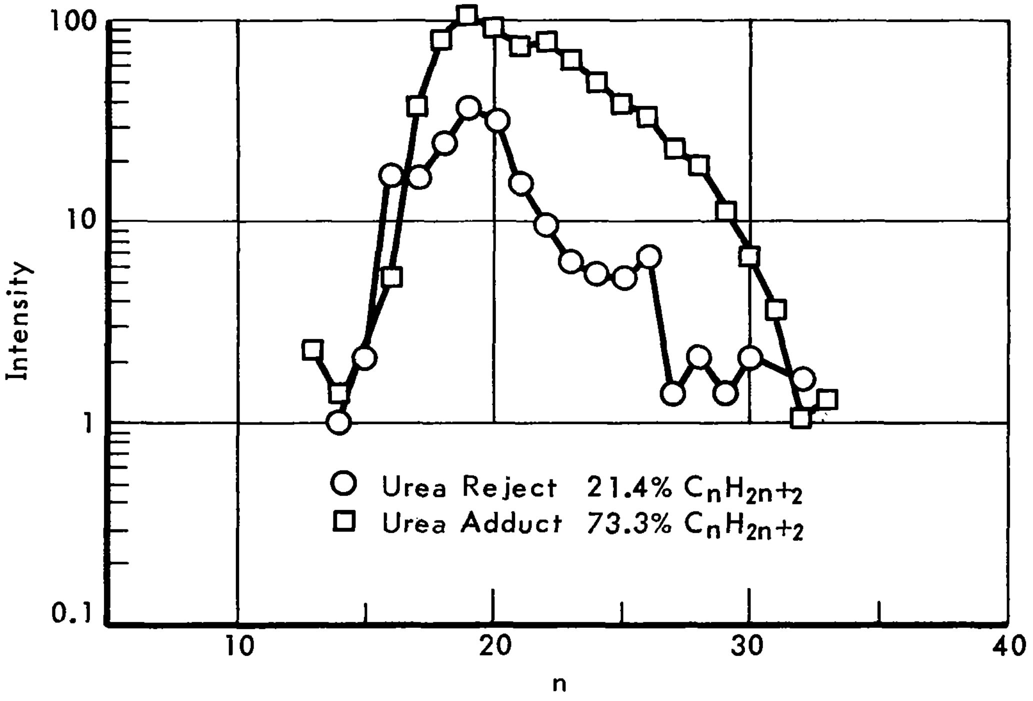

Figure 14. ALKANE ION, $C_nH_{2n+2}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT AND REJECT FRACTIONS OF KALGOORLIE SLATE WP-27

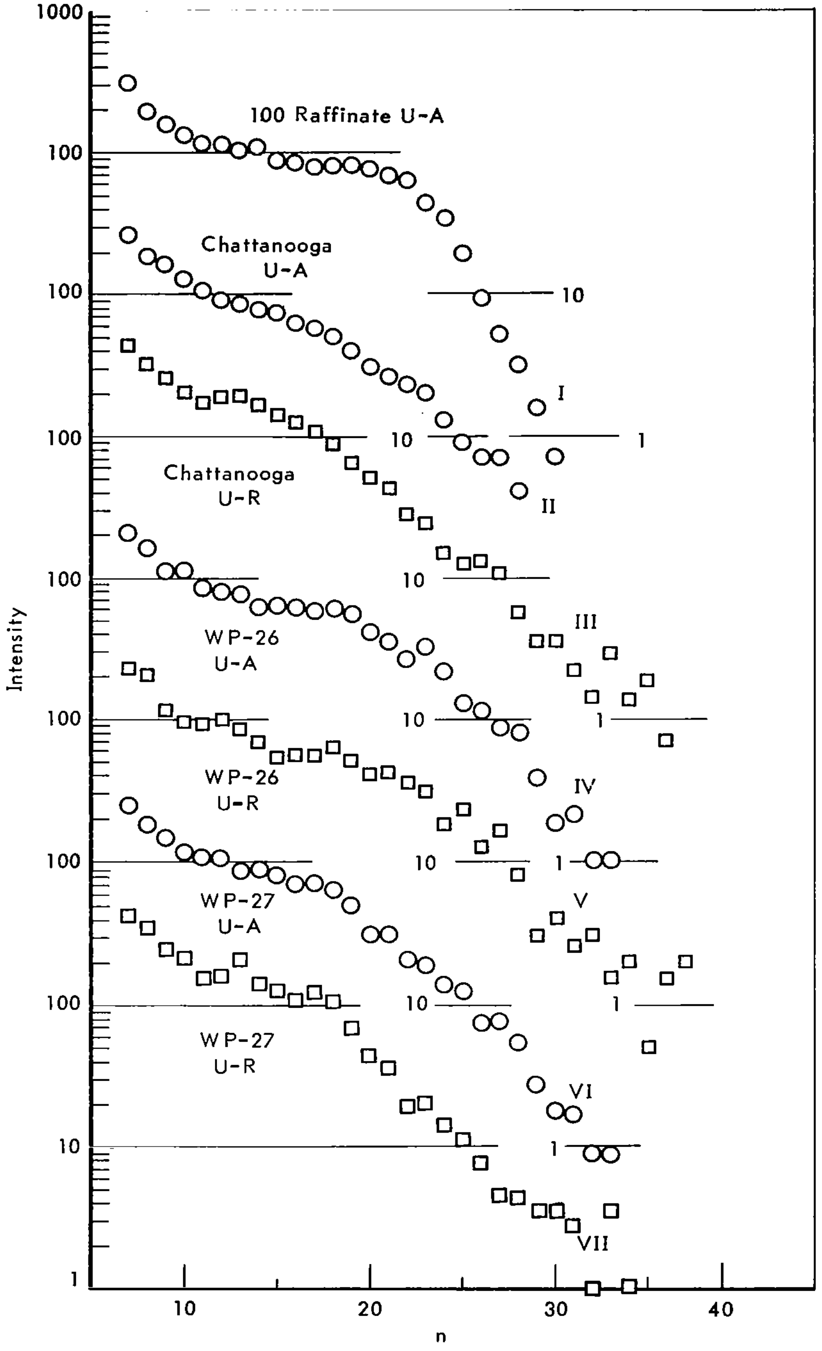

Figure 15. ALKYL ION, $C_nH_{2n+1}^+$, INTENSITY DISTRIBUTION IN, n, OF UREA ADDUCT FRACTION OF 100 RAFFINATE AND THE UREA ADDUCT AND REJECT FRACTIONS OF CHATTANOOGA SHALE, AND KALGOORLIE SLATES WP-26 AND WP-27

U-A = Urea Adduct

U-R = Urea Reject

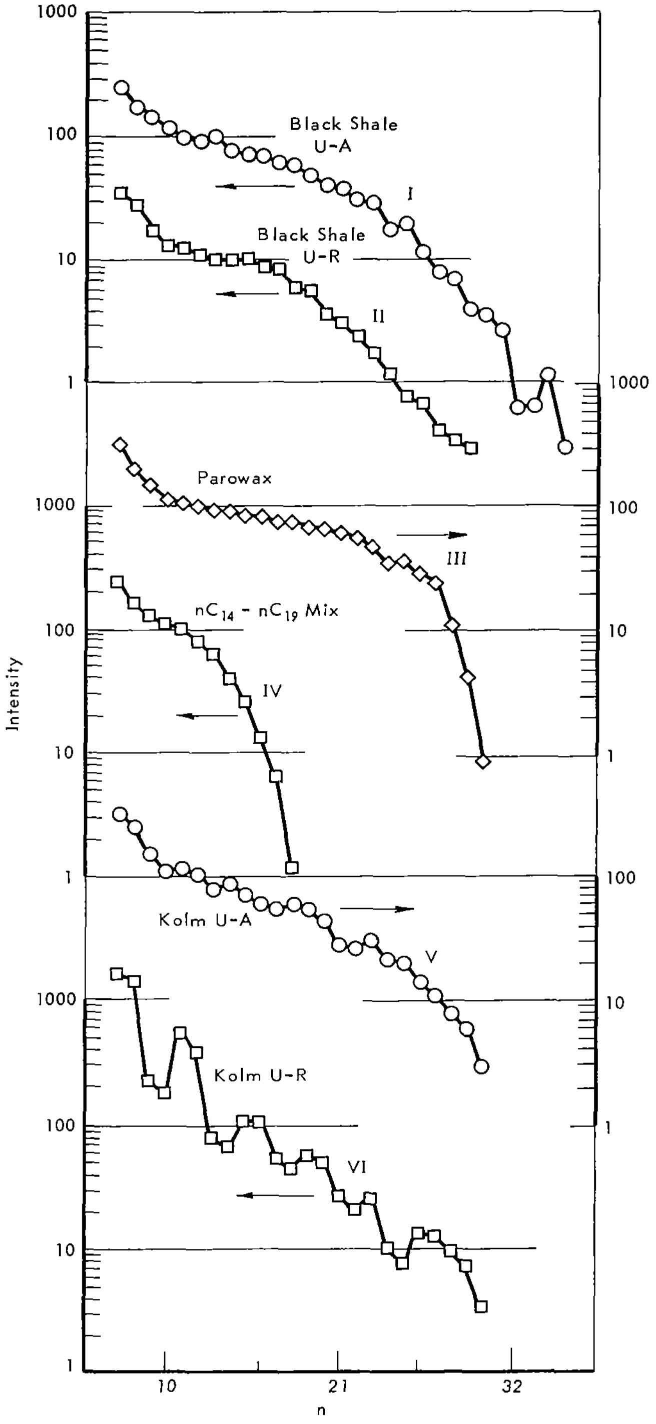

Figure 16. ALKYL ION, $C_nH_{2n+1}^+$, INTENSITY DISTRIBUTION IN, n, OF PAROWAX, A n-ALKANE BLEND, AND THE UREA ADDUCT AND REJECT FRACTIONS OF BLACK SHALE AND BLACK SHALE KOLM

U-A = Urea Adduct

U-R = Urea Reject

that decrease smoothly with increasing n. A random mixture of branched alkanes tends to also give a smoothly decreasing intensity distribution of $C_nH_{2n+1}^+$ ions with increasing n. If there are particularly high concentrations of a single branched alkane or members of a homologous series of branched alkanes (such as the isoprenoids like pristane, phytane, squalane, etc.) in a sample, then in the mass spectrum the $C_nH_{2n+1}^+$ intensity distribution will show maxima above and minima below the smoothly decreasing distribution characteristic of n-alkanes.

Examination of the $C_nH_{2n+1}^+$ ion intensity distributions presented in Figures 15 and 16 show that the urea adduct fractions (U-A) are indeed primarily n-alkanes plus possibly a random mixture of branched alkanes. While there are indications of particular structures in the $C_nH_{2n+1}^+$ intensity curves for the urea-reject fractions from the slates (Figure 15, V and VII), it is only in the case of this fraction from the Kolm (Figure 16, VI) that there are pronounced intensity anomalies. Referring to Figure 11, where it maybe seen that there are very strong fluctuations on the concentration of branched alkane in carbon number in the urea reject fractions from the Kolm, provides the explanation of the origin of the intensity anomalies in the $C_nH_{2n+1}^+$ curve. That the fluctuations in intensity of the $C_nH_{2n+1}^+$ ion in the Kolm urea reject mass spectrum shows less structure than does the $C_nH_{2n+2}^+$ curve (Figure 11) strongly suggests certain structures of branched alkane to be preferentially found in this sediment. However, the carbon number of the intensity maximum in the $C_nH_{2n+1}^+$ curve (Figure 16, VI) namely n = 11, 12, 16 and 17, suggest these preferential structures are not of the isoprenoid type. The isoprenoids lead to intensity maxima for n equal to 8 + 5 m.

It should be noted that in the cases of the urea rejects from the slate extracts, WP-26 and WP-27 (Figure 15, V and VII) maxima in the $C_nH_{2n+1}^+$ intensity are found at n = 13. Similarly from the urea-reject fraction from the Chattanooga shale (Figure 15, III) but not for the urea-reject fraction from Swedish Black Shale (Figure 16, III).

There are shown in Figures 17, 18 and 19 the distributions in carbon number of the intensities of the ions of empirical formula $C_nH_{2n-6}^+$ found in the mass spectra of the various extracts of terrestrial sedimentary rocks examined under the present contract as well as the previous one, and the extracts of the Murray and Hamlet meteorite specimens received from Brookhaven National Laboratory. These hydrocarbons are of particular interest with respect to their being indications of biogeneic processes. Many years ago Fenske and coworkers[a)] showed that there were particularly high concentrations of optically active hydrocarbons in petroleum fractions containing C_{26}-C_{31} hydrocarbons. It has since been found that the major contributors to optical activity of such heavier fractions of petroleum are saturated hydrocarbons of empirical formulae C_nH_{2n-6} and C_nH_{2n-8} with $27 \leq n \leq 30$. The mass spectral properties of these hydrocarbons with large optical activity separated from petroleum suggest them to have structures based on perhydrocyclopentanophenanthrene, i.e., sterane-like structures.

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a) M. R. Fenske, F. L. Carnahan, J. N. Breston, A. H. Caser and A. L. Rescorla, Ind. Eng. Chem. 34, 638 (1942).

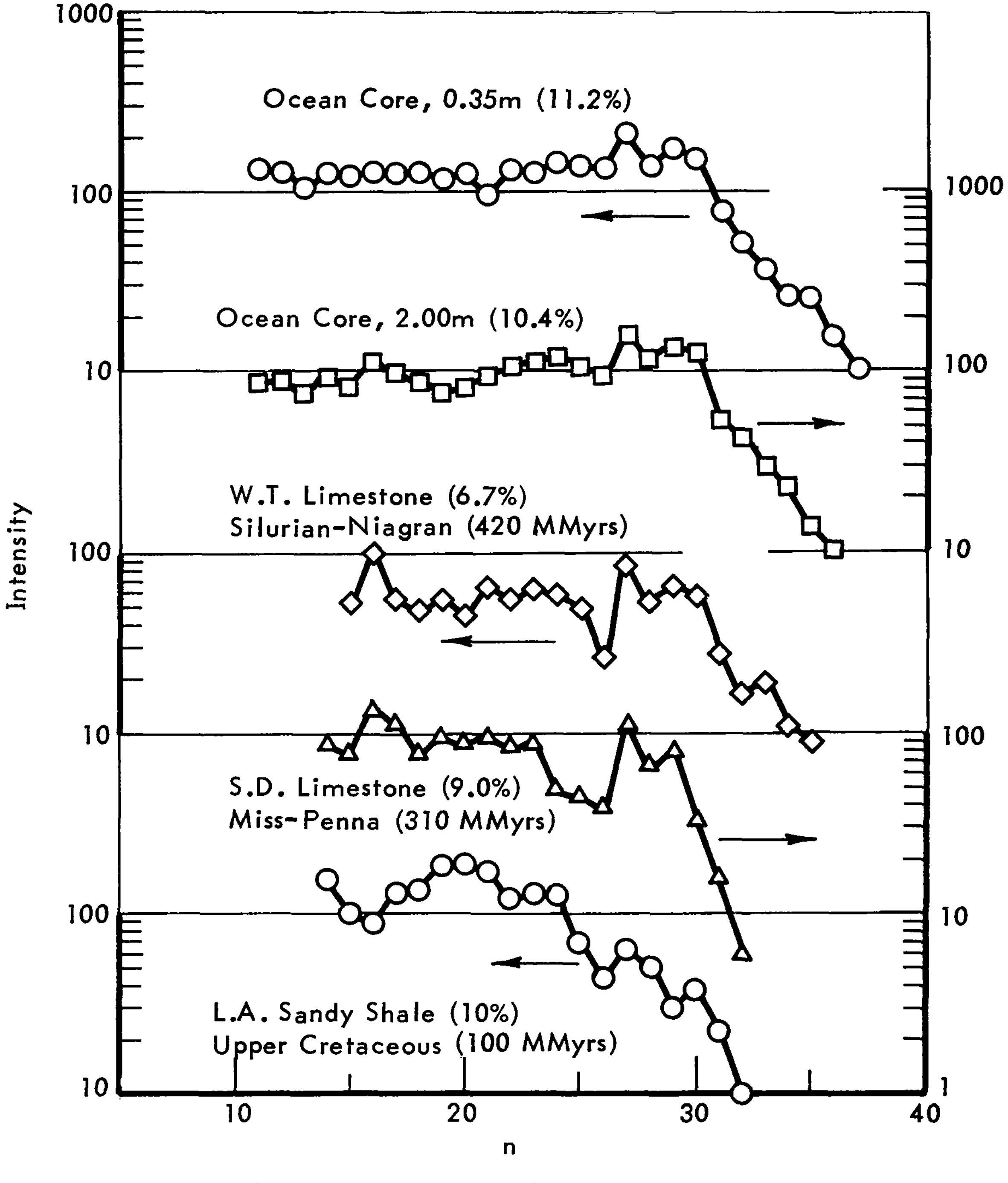

Figure 17. C_nH_{2n-6} ION INTENSITY DISTRIBUTION IN, n, OF TWO OCEAN CORE SEGMENTS, TWO LIMESTONES AND L.A. SANDY SHALE

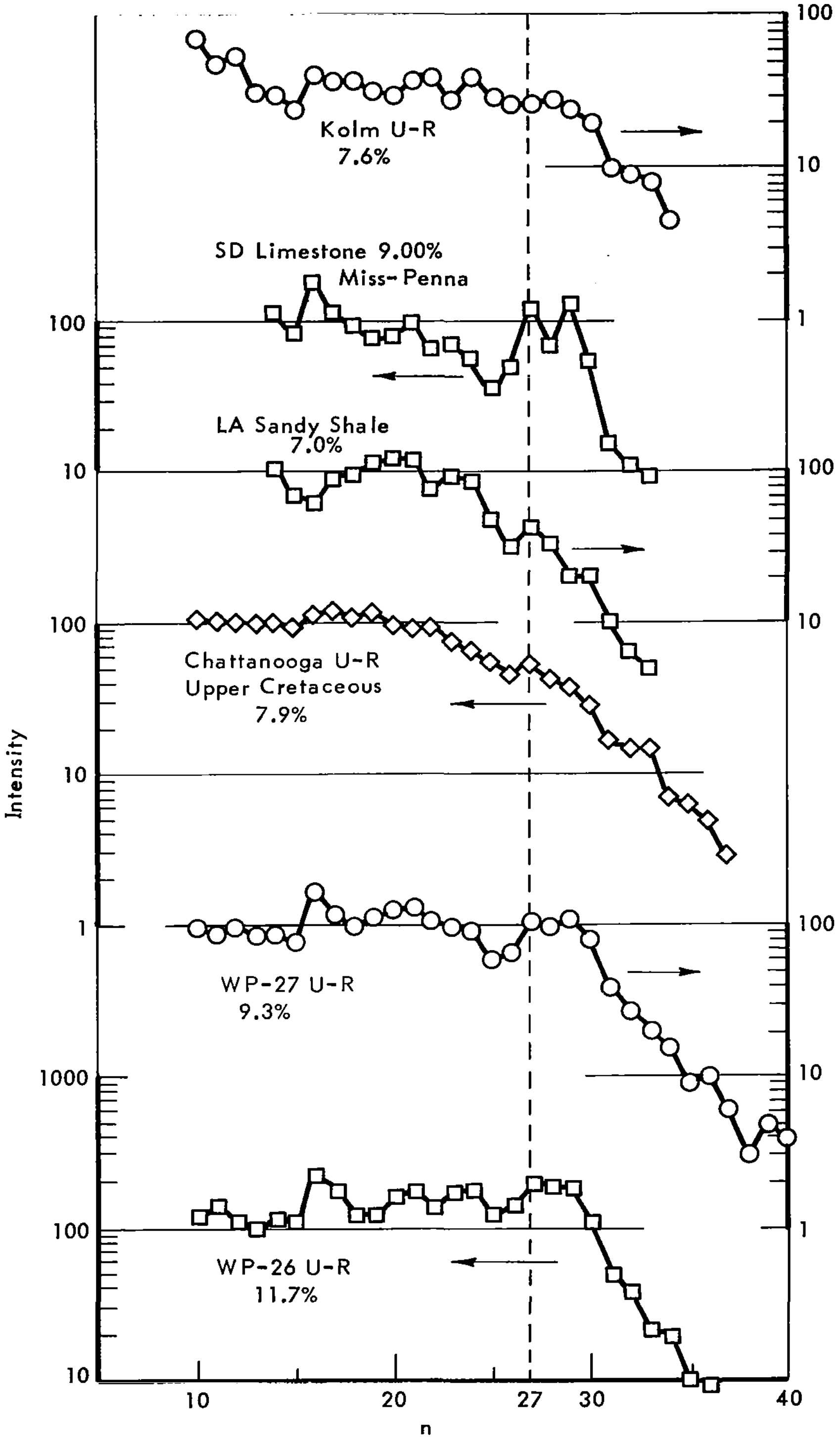

Figure 18. C_nH_{2n-6} ION INTENSITY DISTRIBUTION IN, n, OF TWO LIMESTONES, AND THE UREA REJECT FRACTIONS OF CHATTANOOGA SHALE AND KALGOOELIE SLATES WP-26 AND WP-27

UR = Urea Reject

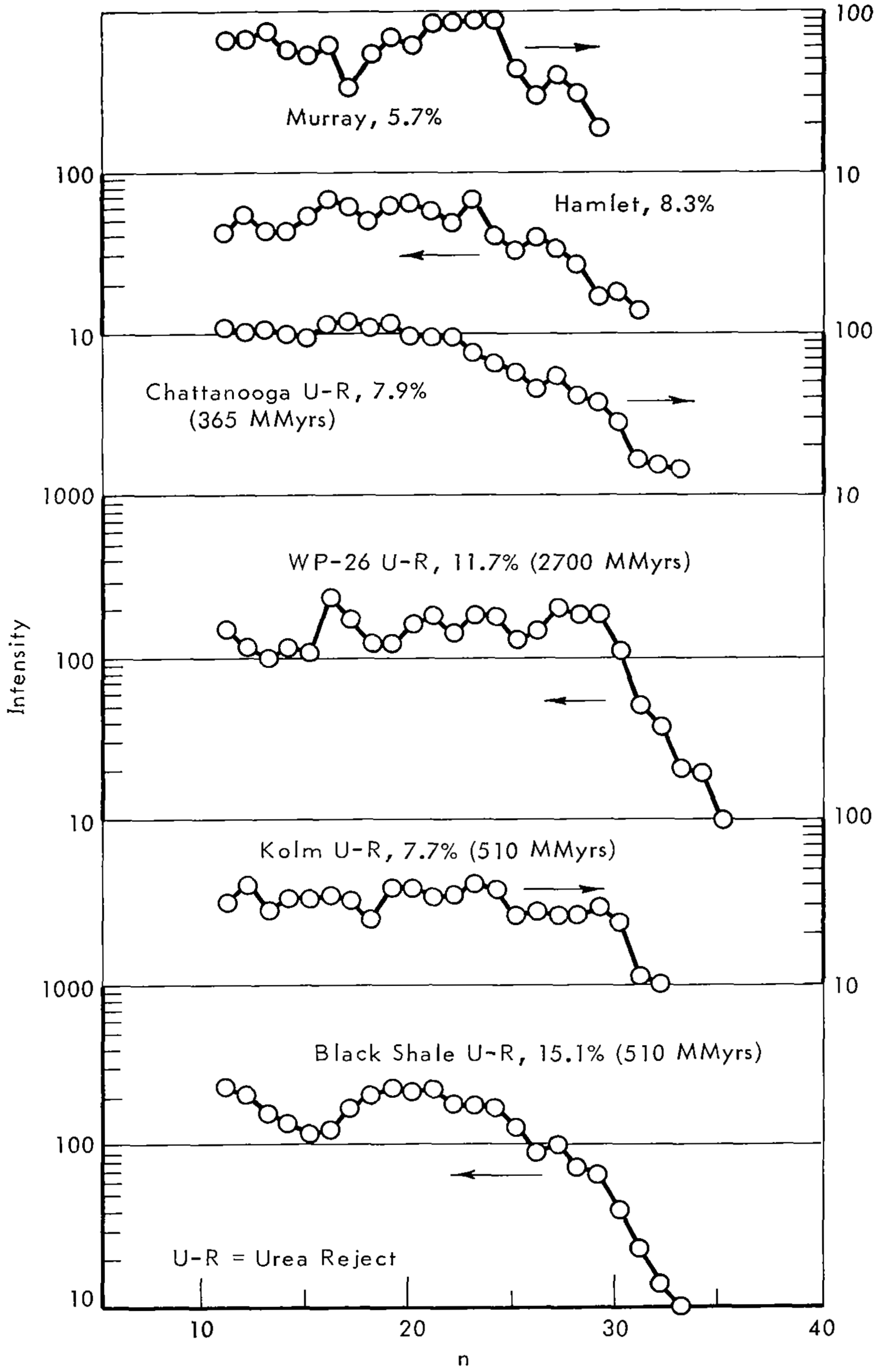

Figure 19. C_nH_{2n-6} ION INTENSITY DISTRIBUTION IN, n, OF METEORITES MURRAY AND HAMLET, AND THE UREA REJECT FRACTIONS OF CHATTANOOGA SHALE, BLACK SHALE, BLACK SHALE KOLM AND KALGOORLIE SLATE WP-26

It has been found that the magnitude of the concentration of the sterane-like, C_nH_{2n-6} hydrocarbons in petroleum varies very widely with the crude oil. The concentrations are usually very small in paraffinic oils, intermediate in naphthenic oils and high in asphaltic oils.

We find in the examination of curves of Figures 17, 18 and 19 that show the distribution of the ions $C_nH_{2n-6}^+$ in the extracts that the terrestrial sediments may be divided into two groups. The various shales ranging in age from 500 to 100 x 10^6 years show relatively low concentrations of C_nH_{2n-6} with $27 \leq n \leq 30$ that are significantly higher than the concentration of C_nH_{2n-6} hydrocarbons of lesser or greater molecular weight, i.e., with $n \leq 26$ or $n \geq 31$. In this respect the extracts from the former group of sediments are like paraffinic petroleum of the "Pennsylvania type", whereas the extracts from the latter group of sediments are like the asphaltic petroleums such as for example, those from the Los Angeles basin.

The extracts from the Murray and Hamlet meteorite specimens show distribution of the ions C_nH_{2n-6} in their mass spectra like that found in the shales, i.e., there is no anomalously large concentration of such ions for $27 \leq n \leq 30$.

Gas Chromatography of Shale and Slate Extracts

Capillary column chromatograms were obtained on all urea adduct and reject fractions of our shale and slate extracts by means of the technique described in an earlier section of this report. Chromatograms of urea rejects ex Black Shale Kolm, and Pyritic Slates WP-26 and WP-27 showed no significant details. The chromatograms of the other fractions are described, using the n-alkane scale of identification, in Tables 13 to 18. Whole numbers in this presentation denote the corresponding n-alkanes; retention volumes of peaks between normals are given as decimal fractions of the emergence difference of the two bracketing normal alkanes. Peak assignments were based on blends of n-alkanes, as well as on the chromatograms of our well characterized gas oil (C_{15} to C_{22}) and Parowax (C_{22} to C_{30}) n-alkane concentrates. n-$C_{17}H_{36}$ was added to the urea-reject fractions to serve as a marker and to facilitate establishing an exact n-alkane scale for these fractions.

n-Alkanes in the chromatograms of the urea adduct fractions appeared with distinct peaks from C_{14} to C_{28}. They showed a smooth distribution with no predominance of species with odd-numbers of carbon atoms. There was no material detected in any of these chromatograms beyond C_{29}. The urea-reject fraction of Black Shale was free of n-alkanes and that of the Chattanooga Shale contained them only in indistinct proportions. The material in the Kolm chromatogram was distributed quite uniformly, but that of the Chattanooga Shale contained several larger and well defined peaks between those of the normals.

In view of the great interest accorded recently to the presence of isoprenoid isoalkanes in extracts of sedimentary rocks,[a] attempts were made to detect these materials in our samples. In a strict sense, true isoprenoids are those structures which are multiples of the isoprene unit, such as farnesane (2,6,10-trimethyldodecane), phytane (2,6,10,14-tetramethylhexadecane), squalane ($C_{30}H_{62}$), carotenes (C_{40}-structures). In a broader sense, however, all alkanes possessing methyl groups in the 2,6,10,14,18-, etc. positions are included in this definition. This latter group of structures may result from degradative processes which attack the main hydrocarbon chain at the end that carries the ethyl group.

Three isoprenoid isoalkanes, farnesane, phytane and pristane (2,6,10,14-tetramethylpentadecane) were available to us in reasonable purity. Their retention volumes, obtained in our silicone oil-coated capillary column and expressed in the normal alkane scale, were as follows: farnesane, 13.8; pristane, 16.87; and phytane, 17.92. None of the chromatograms of the five shale and slate sample extracts showed any material in the vicinity of the farnesane retention volume. Peaks in the vicinity of the pristane and phytane retention volumes were found in three chromatograms: urea reject of Chattanooga Shale (Table 17), 16.85 and 17.77; urea adduct of Chattanooga Shale (Table 12), 16.85 and 17.89; and urea adduct of Kalgoorlie Slate WP-26 (Table 15), 16.84 and 17.92. With the exception of the 17.77 peak, all the other may be considered to correspond to one or the other of our two model compounds. Thus, Chattanooga Shale may contain as much as 5.5% pristane and 0.7% phytane although it is likely that these peaks are mixtures of several components. The maximum values for the WP-26 slate are: pristane, 0.4%; phytane, 0.3%.

The mass spectrometric evidence for the presence of isoprenoid structures in these materials was discussed in an earlier section of this report. It was noted that isoprenoids lead to intensity maxima for n equal to 8 + 5 m in the $C_nH_{2n+1}^+$ curve. Such maxima were found for both the Chattanooga Shale and Kalgoorlie Slate WP-26 extracts (see Figure 15, III and V).

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[a] W. G. Meinschein, E. S. Barghorn and J. W. Schopf, Sci. 145, 262 (1964); G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame and M. Calvin, ibid. 145, 263 (1964); T. Belsky, R. B. Johns, E. D. McCarthy, A. L. Burlingame, W. Richter, and M. Calvin, Nature 206, 446 (1965).

Table 12. CHROMATOGRAM OF THE UREA ADDUCT FRACTION OF CHATTANOOGA SHALE

Retention Volume, n-Alkane Scale	Area, sq in.
13.00	0.252
unresolved region	-
14.00	0.162
14.47	0.011
14.58	0.016
14.69	0.006
14.76	0.005
15.00	0.254
15.45	0.024
15.58	0.034
15.68	0.022
15.78	0.011
16.00	0.258
16.40	0.018
16.46	0.008
16.56	0.023
16.68	0.018
16.84[a]	0.028 (0.7%)
17.00	0.250
17.21	0.019
17.41	0.031
17.55	0.025
17.67	0.015
17.89[b]	0.029 (0.7%)
18.00	0.220
18.17	0.019
18.38	0.039
18.56	0.032
18.69	0.018
18.89	0.010
19.00	0.197
19.32	0.010
19.42	0.007
19.54	0.023
19.69	0.016
19.89	0.004
20.00	0.173
20.36	0.015
20.55	0.013
20.69	0.017
20.83	0.009
21.00	0.191
21.33	0.036
21.54	0.027
21.69	0.013
22.00	0.169
22.34	0.042
22.55	0.023
23.00	0.176
23.31	0.029
23.54	0.007
23.67	0.024
24.00	0.174
24.36	0.023
24.50	0.021
24.74	0.021
25.00	0.144
unresolved region	-
25.71	0.036
26.00	0.156
unresolved region	-
27.00	0.180
unresolved region	-
28.00	0.148
n-alkanes, total	3.104 78.0%
isoalkanes, total	0.877 22.0%
Total	3.981 100.0%

[a] Pristane (?).

[b] Phytane (?).

Table 13. CHROMATOGRAM OF THE UREA ADDUCT FRACTION OF BLACK SHALE KOLM

Retention Volume, n-Alkane Scale	Area, sq in.	Retention Volume, n-Alkane Scale	Area, sq in.
16.00	0.035	22.00	0.127
unresolved region	-	22.32	0.013
17.00	0.057	22.58	0.017
unresolved region	-	22.74	0.024
18.00	0.073	23.00	0.477
unresolved region	-	23.10	0.527
19.00	0.087	23.27	0.017
19.20	0.019	23.57	0.019
unresolved region	-	23.74	0.027
20.00	0.104	24.00	0.206
20.34	0.038	unresolved region	-
unresolved region	-	25.00	0.163
21.00	0.076	unresolved region	-
21.12	0.168	26.00a)	0.106
unresolved region	-		

a) Very little material in chromatogram beyond n-C_{26}.

Table 14. CHROMATOGRAM OF THE UREA ADDUCT FRACTION OF BLACK SHALE

Retention Volume, n-Alkane Scale	Area, sq in.
13.00	0
14.00	0
15.00	0.011
16.00	0.012
17.00	0.023
18.00	0.006
19.00	0.007
20.00	0.010
21.00	0.014
22.00	0.023
22.46	small; indistinct
23.00	0.015
24.00	0.039
25.00	0.033
25.27	small; indistinct
25.72	small; indistinct
26.00	0.046
26.40	indistinct
27.00	0.020

Table 15. CHROMATOGRAM OF THE UREA ADDUCT FRACTION OF PYRITIC SLATE WP-26

Retention Volume, n-Alkane Scale	Area, sq in.	Retention Volume, n-Alkane Scale	Area, sq in.
13.00	very small	23.65	0.006
14.00	very small	23.74	0.010
15.00	0.052	23.84	0.007
16.00	0.038	24.00	0.138
16.84a)	0.005 (0.4%)	24.26	0.014
17.00	0.063	24.36	0.024
17.92b)	0.004 (0.3%)	24.50	0.013
18.00	0.068	24.65	0.015
19.00	0.062	unresolved region	-
20.00	0.066	25.00	0.126
20.56	0.008	25.41	0.015
21.00	0.086	unresolved region	-
21.73	0.022	26.00	0.108
21.88	0.029	26.25	0.022
22.00	0.153	unresolved region	-
22.30	0.023	27.00	0.112
22.44	0.008	28.00	0.046
23.00	0.154	29.00	very small

a) Pristane (?).
b) Phytane (?).

Table 16. CHROMATOGRAM OF THE UREA ADDUCT FRACTION OF PYRITIC SLATE WP-27

Retention Volume, n-Alkane Scale	Area, sq in.
16.00	0
17.00	0.024
18.00	0.077
18.60	very small
19.00	0.112
20.00	0.085
20.56	very small
21.00	0.077
22.00	0.077
22.72	very small
23.00	0.038
23.28	very small
24.00	0.035
25.00	0.030

Table 17. CHROMATOGRAM OF THE UREA REJECT FRACTION OF CHATTANOOGA SHALE

Retention Volume, n-Alkane Scale	Area, sq in.
13.00	0
13.16	0.022
13.66	0.055
14.00	0.270
unresolved region	-
14.48	0.264
14.56	
14.70	0.021
unresolved region	-
14.91	0.031
15.00	0.211
unresolved region	-
15.30	0.022
15.43	0.098
15.53	0.097
15.67	0.060
15.80	0.059
15.88	0.022
16.00	0.414
16.21	0.099
16.34	0.158
16.41	0.133
16.48	
16.55	0.079
16.59	
unresolved region	-
16.85[a]	0.236 (4.8%)
17.00	market added
17.17	0.058
17.25	
17.32	0.056
17.44	0.149
17.58	0.053
17.77	0.047
18.00	0.174
18.10	0.166
18.37	0.098
18.47	0.032
18.59	0.079
18.77	0.042
18.89	0.046
19.00	0.022
19.08	0.136
19.25	0.069
19.31	0.033
19.40	0.044
19.46	0.135
19.51	
19.62	0.074
19.78	0.100
20.00	0.046
20.09	0.122
20.23	0.066
20.36	0.083
20.49	0.068
20.65	0.101
20.79	0.093
21.00	0.012
21.07	0.064
unresolved region	-
21.43	0.084
21.48	
21.59	0.066
21.85	0.107
22.00[b]	0.025

a) Pristane (?).

b) Beyond n-C_{22}, there is little material in the chromatogram and not resolved enough for measurement.

Table 18. CHROMATOGRAM OF THE UREA REJECT FRACTION OF BLACK SHALE

Retention Volume, n-Alkane Scale	Area, sq in.
17.00	(marker added)
18.00[a]	very small
18.72	0.077
19.00	0.013
19.45	0.068
19.95	0.040
20.00	0.015
20.33	0.101
20.71	0.080
21.00	0.082
21.33	0.083
21.90	0.025
22.00	very small

a) Identification of n-alkanes beyond C_{17} is somewhat uncertain.

Mass Spectrometry of Meteorite Extracts

The mass spectra obtained of the hexane extract fraction from the Murray and Hamlet meteorite specimens (see Table 9) were interpreted by the modified parent peak method to yield the distribution of hydrocarbons in empirical formula shown in Table 19. Comparison of these data with those shown earlier in Table 11 reveals the hydrocarbon distribution in empirical formula of the extracts from these meteorite specimens to be most like that previously found for the old Kalgoorlie slate, WP-27, the shallower of the two slate specimens.

Table 19. DISTRIBUTION IN EMPIRICAL FORMULA OF SATURATES PLUS MONOAROMATIC HYDROCARBONS OF MURRAY AND SATURATED HYDROCARBONS OF HAMLET

Hydrocarbons	%V	
	Murray	Hamlet
C_nH_{2n+2}	42.0	38.5
C_nH_{2n}	24.0	19.2
C_nH_{2n-2}	13.7	14.9
C_nH_{2n-4}	7.8	10.5
C_nH_{2n-6}	5.7	8.5
C_nH_{2n-8}	3.8	4.8
C_nH_{2n-10}	3.0	3.5

There are shown in Figure 20 the distribution in carbon number, n, of the intensity of the alkane ($C_nH_{2n+2}^+$) and alkyl (C_nH_{2n+1}) ions in the mass spectra. The distributions of the $C_nH_{2n+2}^+$ ions in n are very much more irregular for the meteorite extracts than was found in any of the urea complex fractions from the terrestrial sediments extracts. Several of the urea rejects, particularly three from the Kolm and the deeper Kalgoorlie slate (WP-26), show similarly irregular distribution in molecular weight of alkane ions.

To the extent that an irregular distribution in molecular weight in a homologous series of compounds such as the alkanes may be deemed to be a criterion for biogenic synthesis of the compounds, one would be inclined to infer that there is stronger evidence for the biogenic origin of the alkanes extracted from the meteorite specimen than is the case for any of the terrestrial sediments.

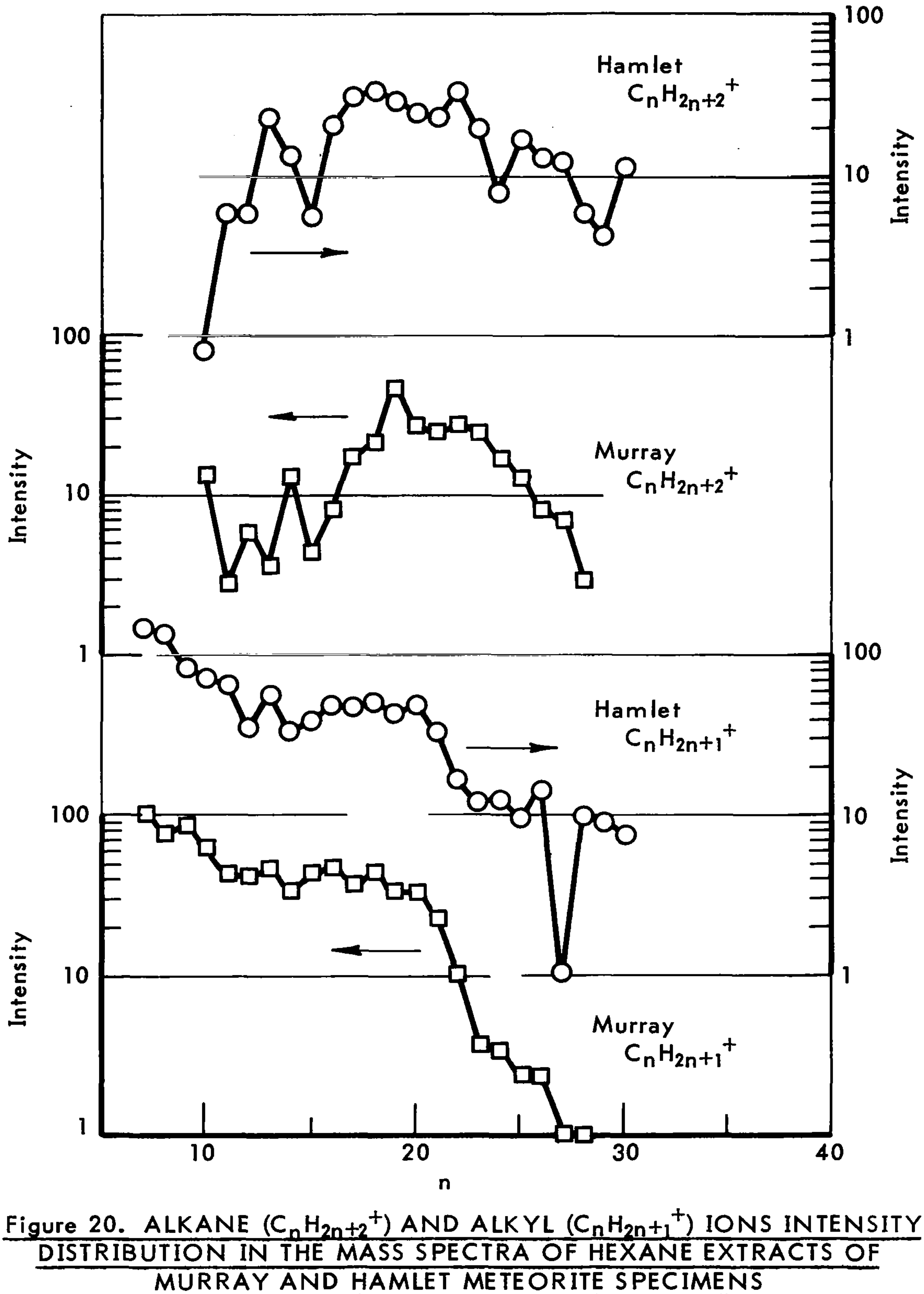

Figure 20. ALKANE ($C_nH_{2n+2}^+$) AND ALKYL ($C_nH_{2n+1}^+$) IONS INTENSITY DISTRIBUTION IN THE MASS SPECTRA OF HEXANE EXTRACTS OF MURRAY AND HAMLET METEORITE SPECIMENS

The distribution of intensity of alkyl ion in molecular weight in the meteoric extracts is also more irregular than in the case of any of the extracts from terrestrial sediments. In particular the mass spectrum of the Hamlet saturates shows a well defined maximum at $n = 13$, that is usually taken as presumptive evidence for the presence of alkanes with isoprenoid structures.

The distribution of intensity in carbon number of the ion, $C_nH_{2n-6}^+$, of the mass spectra of these meteorite specimen extracts were shown in Figure 17 and have been discussed in connection with the distribution of these ions in the mass spectra of the terrestrial sediment extracts.

Direct Mass Spectrographic Examination of Four Meteoritic Samples

It has been mentioned above that the quantities of the Bruderheim, Felix, Murray and Orgueil meteoritic material received from Professor Calvin's laboratory, ca 200 mg of each as powder, were deemed too small to warrant the application of the solvent extraction techniques for the examination for organic chemical substances in general and/or hydrocarbons in particular. As a consequence these materials were examined for volatile constituents mass spectrographically employing the direct inlet system of the C.E.C. 21-110 mass spectroscope and the photographic plate recording system. The order of 20 mg of the as received powder material was charged to the probe and a series of 5 to 10, 2 to 4 minute exposures of the mass spectrum made as the temperature of the sample probe was raised from ambient to 220°C. In the cases of the Murray and Orgueil samples the mass spectrum of a partially deuterated C_{18} normal alkane was simultaneously recorded in order to provide a precise mass scale, while for the Bruderheim and Felix samples mass spectra of n-heptane and a mixture of C_{14}-C_{19} normal alkanes provided the precision mass scale. The hydrocarbon mass markers were introduced through the conventional reservoir-effusive leak system.

In order to obtain a measure of the sensitivity of the direct inlet-mass spectrographic technique in the detection of organic constituents of mineral matter, a similar 20-mg sample of unextracted Kalgoorie slate, WP-26, was examined by the same technique. This sample (WP-26) has been reported in a previous section to contain the order of 12 ppm hexane soluble material that can be eluted from silica gel, plus an additional 200 ppm of substances extractable by benzene/methanol.

The mass spectra of the vapors drived from the solid (WP-26) showed no evidence of the C_{14}^+ saturated hydrocarbons found in the hexane extract, although there was evidence of lower molecular weight alkanes, particularly C_8H_{18} and C_9H_{20}, and alkenes (or cycloalkanes), $C_{12}H_{24}$, $C_{13}H_{26}$ and $C_{14}H_{28}$. There was found evidence for the presence of both naphthalene and methyl naphthalene as well as other unsaturated C_{10}-C_{14} hydrocarbons with unsaturation between those of the benzene homologous and those of naphthalene.

Although sulfur vapor was observed as the ions S_3^+, S_4^+, S_5^+, S_6^+, S_7^+ and S_8^+, and there was found H_2S_2, CS_2 and SO_2 (partially resolved from the S_2 ion) there was virtually no evidence of sulfur containing organic compounds other than possibly traces of methyl and ethyl (or dimethyl) thiophene.

The more intense ions in the mass spectrum were found to be those containing O, O_2, NO and NO_2 in addition to C and H. The most intense of the higher molecular weight ions found was of nominal m/q = 256, and exact 256.242 ± 0.004, that may be assigned with confidence to the formula $C_{16}H_{32}O_2$ (m/q = 256.240). There was also at nominal m/q = 257 (257.246 ± 0.005) an ion of about one-half the intensity of the m/q = 256 ion to which one can assign the formula $C_{16}H_{33}O_2$ (257.248). The precise determination of the mass-to-charge ratio of these ions was possible because of the proximity of the S_8^+ (255.7766). The ion $C_{16}H_{32}O_2^+$ and $C_{16}H_{33}O_2^+$ are characteristic of the mass spectra of the long chain alcohol esters of palmitic acid.

There were observed also at one-third to one-fourth the intensity of m/q = 256, ions with nominal m/q = 285, 270, 242 and 228 that one is inclined to attribute to the presence of esters of homologues of palmitic acid. The absence from the spectrum of nearby ions of precisely known m/q does not permit assignment of exact m/q to this group of ions.

Of comparable intensity to the ions to which we provisionally assign the formulae, $C_{18}H_{36}O_2$ (m/q = 284), $C_{17}H_{34}O_2$ (m/q = 270), $C_{15}H_{30}O_2$ (m/q = 242), and $C_{14}H_{28}O_2$ (m/q = 228), was one at m/q = 236. If the assignments of formulae of the ions of m/q = 228 and 242 are correct, we find 236.20 ± 0.10 for the precise mass of this ion that would admit any of the following likely formulae: $C_{16}H_{28}O$ (236.214), $C_{15}H_{26}NO$ (236.201), $C_{15}H_{24}O_2$ (236.178), $C_{17}H_{32}$ (236.250). Possibly homologous ions, i.e., m/q = 250 and m/q = 222 were absent from the mass spectrum.

Another "high" molecular weight ion of intensity comparable to those under discussion was m/q = 213 for which we find the exact mass 213.13 ± 0.05 by lengthy extrapolation from the Hg^{204} ion in the "background". The value found for the precise mass corresponds closely to that of the formula, C_{15} $C_{15}H_{17}O$ (213.128).

At m/q = 199 and 185 there were found ions at one-half and the same intensity respectively as that of m/q = 213. The precise m/q of the first of these is well fixed as 199.159 ± 0.003 by the adjacent Hg^{199} ion while the latter is less well fixed at 185.17_2 ± 0.01 by extrapolation from the S_6 ion at m/q = 191.833. Probable assignments for these ions are $C_{11}H_{21}NO_2$ (199.157) and $C_{11}H_{23}NO$ (185.178).

Orgueil

There are shown in Figures 21, 22 and 23 the reproduction of mass spectra obtained of the volatile constituents that could be driven from the specimen of the Orgueil meteorite. Figure 21 shows the complete mass spectrum obtained with a relatively wide slit to increase the effective sensitivity. Figure 22 is an enlargement of a portion of the spectral plate shown in Figure 21. Figure 23 is an enlargement of the high molecular weight range portion of the spectrum obtained with a relatively narrow slit and a separate sample from our specimen of this meteorite.

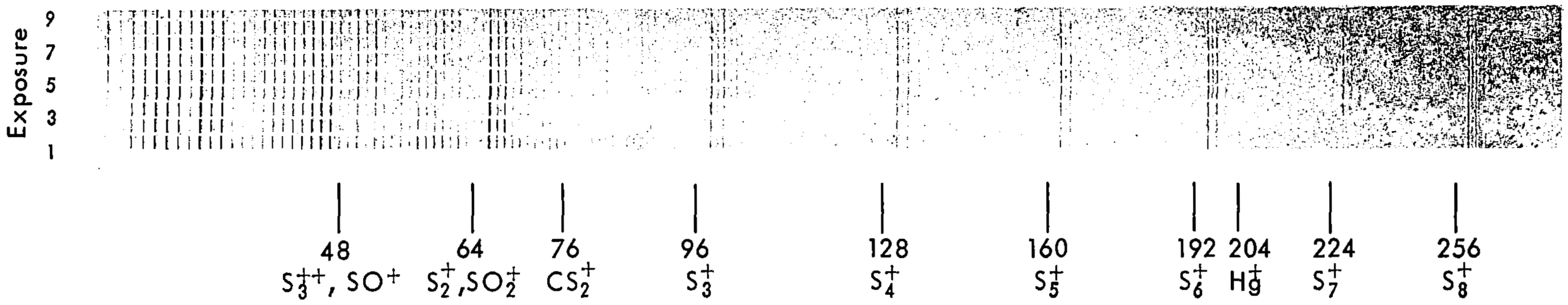

Figure 21. DIRECT INLET MASS SPECTRUM EX "ORGUEIL"

Temperature increases from 75 to 225°C from exposure 1 to Exposure 9

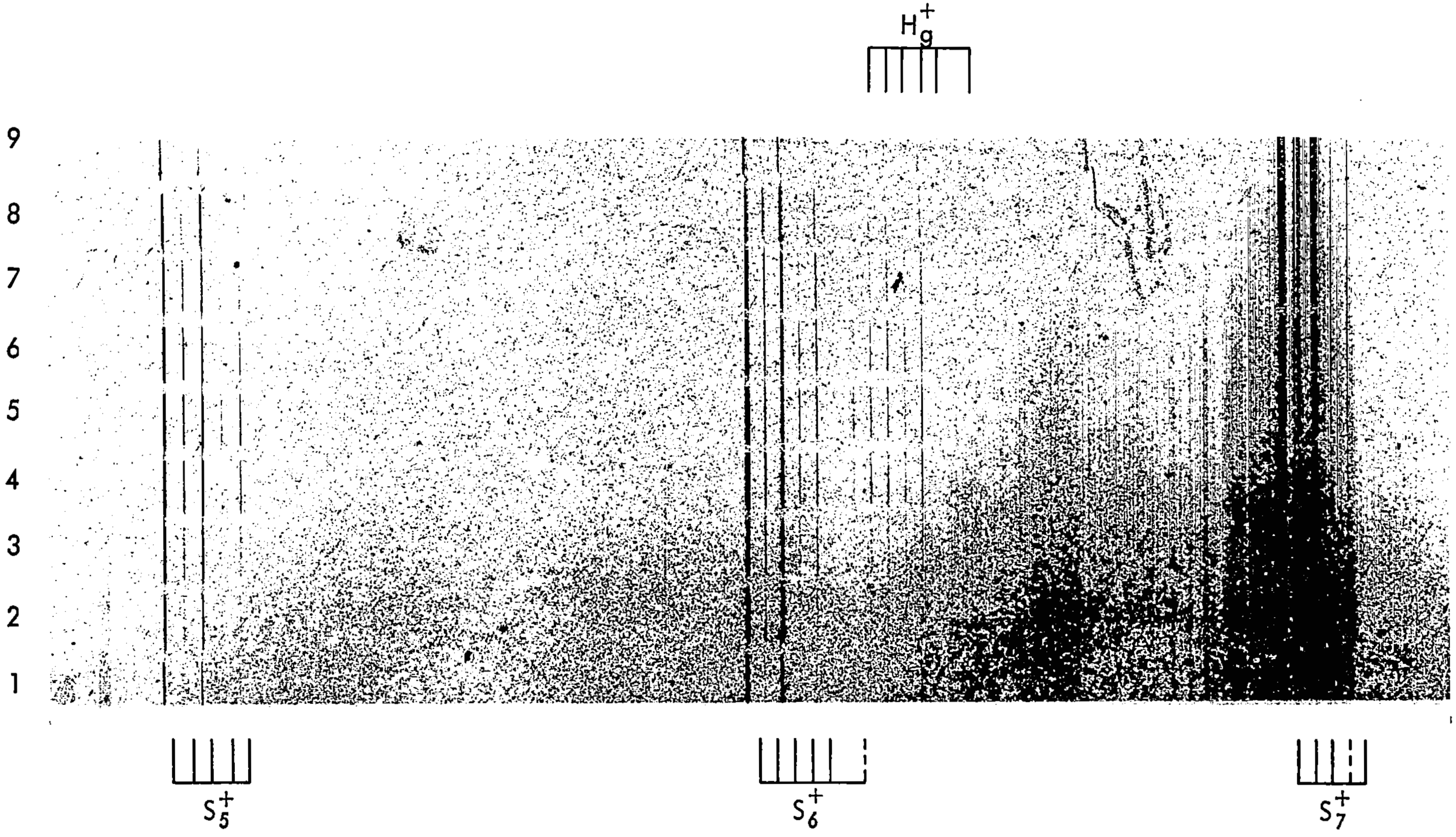

Figure 22. DIRECT INLET MASS SPECTRUM EX ORGUEIL

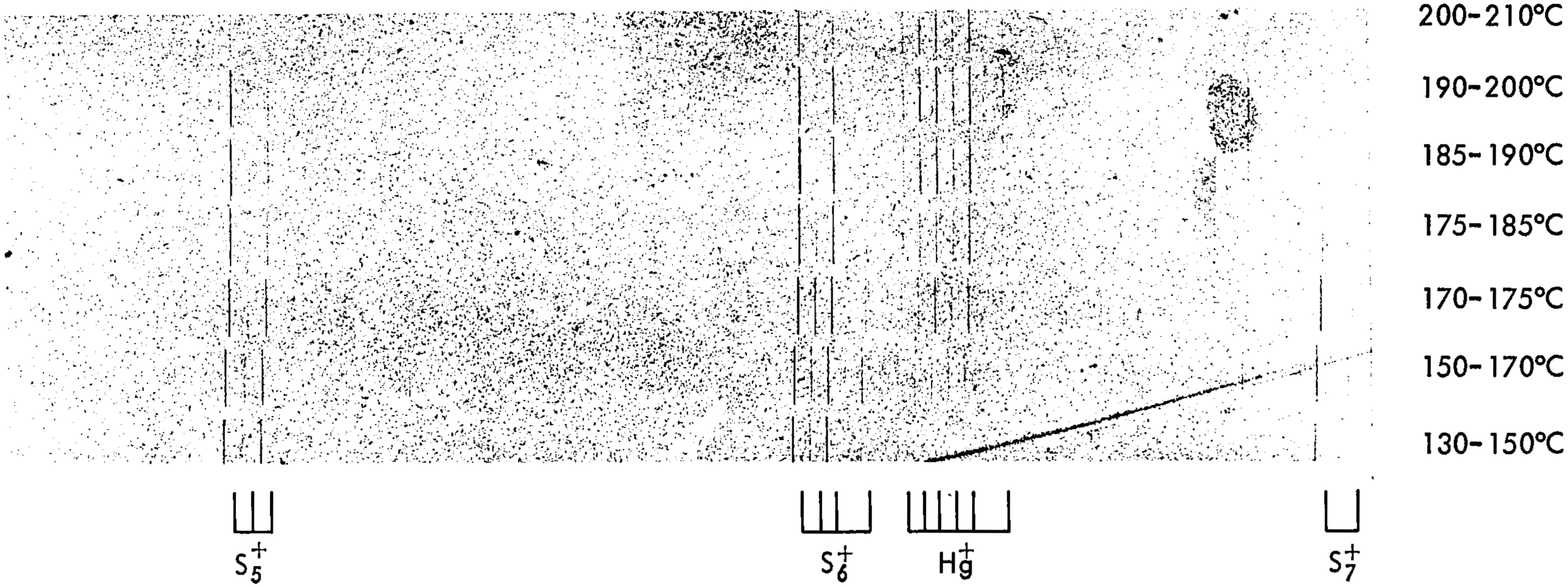

Figure 23. DIRECT INLET MASS SPECTRUM EX ORGUEIL "NARROWER SLITS"
The Temperature of the Specimen for the Various Mass Spectral Exposures is Shown at the Right

The only volatile substances with molecular weight greater than 100 to be found indicated in Figure 27 are the sulfur allotropic ions, S_4^+, $S_5,^+$ S_6^+, S_7^+ and S_8^+ and mercury. Below molecular weight 100 there is clear evidence of the presence of a variety of unsaturated hydrocarbons and CS_2 and SO_2.

That the mercury found in the mass spectra is from the meteorite specimen, not instrument background, may be concluded from examination of the enlargements shown in Figures 22 and 23. In both cases it is seen that the intensity of the mercury isotopic lines increase as the sample temperature was increased.

We find no evidence for the higher molecular weight hydrocarbons that have been found in specimens of other stones this fall.

Felix

The direct mass spectrometric examination of the volatile substances associated with the Felix meteoritic specimen revealed our sample to have a relatively high concentration of a wide variety of such substances. It would appear that an important source of these volatile substances is contamination, since the fall. There are found in the mass spectrum the substances $C_{10}H_5Cl_3$, $C_{10}H_4Cl_4$ and $C_{10}H_3Cl_5$, probably tri-, tetra, and pentachloronaphthalene, respectively.

An enlargement of a portion of one of the mass spectral plates obtained for this specimen is shown in Figure 24. Across the top of the plate there are numbered the lines due to the principal isotopic species of normal alkane ions, a C_{14}-C_{19} n-alkane mixture was added to provide a precision mass scale after several exposures had been made of the mass spectrum of the meteoritic vapors. Across the bottom of the plate there are marked the multiplets that were identified as the polychlorohydrocarbon. Preliminary identification of these lines was based on the nominal molecular weights, the number and relative intensity of the multiplet lines. Final confirmation of the formulae assignments were made from the precise molecular weights of the ions as shown in Table 20.

Careful examination of the reproduction of the mass spectral plate shown in Figure 24, particularly the spectral bands labeled 6 and 7, indicates the probable presence of a dibromo compound at nominal molecular weights 290, 292 and 294.

It is of interest to speculate on the source of the $C_{10}H_xCl_8$ substances found in this specimen. For a period between 1930 and 1940 polychloronaphthalenes, under the trade name, Halowax, were used as plasticizers and extenders for surface coatings. It seems not improbable that such coatings may have been used on a museum cabinet in which the Felix specimen was stored and the contamination arose through vapor transfer.

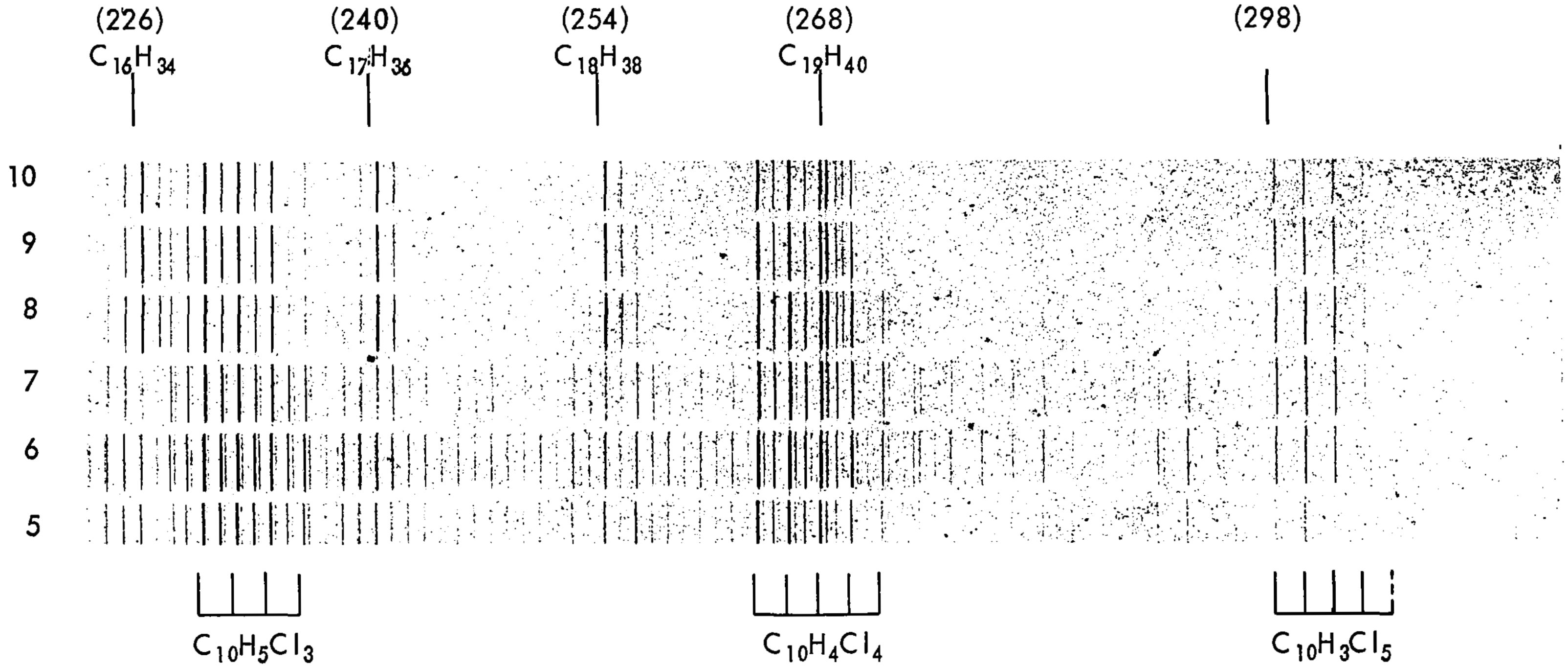

Figure 24. DIRECT INLET MASS SPECTRUM EX "FELIX"

Table 20. IDENTIFICATION OF CHLORO COMPOUNDS IN FELIX METEORITE

Nominal m/q	Observed m/q	Calculated for	
230	229.957 ± 0.012	229.946	$C_{10}H_5Cl_3{}^{35}$
232	231.959 ± 0.012	231.943	$C_{10}H_{25}Cl^{35}_{2}Cl^{37}$
234	233.962 ± 0.012	233.940	$C_{10}H_5Cl^{35}Cl^{37}_{2}$
236	235.934 ± 0.012	235.937	$C_{10}H_5Cl^{37}_{3}$
264	263.917 ± 0.003	263.907	$C_{10}H_5Cl^{35}_{4}$
266	265.914 ± 0.003	265.904	$C_{10}H_4Cl^{35}_{3}Cl^{37}_{2}$
268	267.917 ± 0.003	267.901	$C_{10}H_4Cl^{35}_{2}Cl^{37}_{2}$
270	269.903 ± 0.003	269.898	$C_{10}H_4Cl^{35}Cl^{37}_{3}$
272	271.862 ± 0.003	271.895	$C_{10}H_4Cl^{37}_{3}$
298	297.83 ± 0.03	297.868	$C_{10}H_3Cl^{35}_{5}$
300	299.82 ± 0.03	299.865	$C_{10}H_3Cl^{35}_{4}Cl^{37}$
302	301.83 ± 0.03	301.862	$C_{10}H_3Cl^{35}_{3}Cl^{37}_{2}$
304	303.80 ± 0.03	303.859	$C_{10}H_3Cl^{35}_{2}Cl^{37}_{3}$
306	305.81 ± 0.03	305.856	$C_{10}H_3Cl^{35}Cl^{37}_{4}$

Bruderheim and Murray

The application of the direct mass spectrometric technique to 20 mg sample of the Murray and Bruderheim specimens received from Professor Calvin's Laboratory gave results similar to those for the Orgueil specimens in that evidence was found for only low molecular weight ($\leq C_7$) unsaturated hydrocarbons and simple sulfur compounds. The mass spectrum from the Murray specimen showed free sulfur vapor to be volatilized but at much lower partial pressure than from Orgueil while no free sulfur was observed in the case of Bruderheim. The sulfur compounds that were identified included SO_2, COS and CS_2.

Optical Absorption Spectra

Ultraviolet absorption spectra were obtained of dioxane solutions of the benzene eluates from the silica gel chromatography of extracts of the three shale specimens, the two slate specimens and the Hamlet meteorite. The spectrum of the Hamlet extract along with four typical terrestrial sediment extracts are shown in Figure 25. The spectrum of the Hamlet extract differs very markedly from the terrestrial sediment extracts which are very similar to the spectra of petroleum fractions in the lubricating oil range of molecular weight. The Hamlet extract shows well defined absorption maxima at λ = 2730, 2875, 3200 and 3360 A. These are unquestionably indicative of particular structure of aromatic hydrocarbons but we do not know what these structures are.

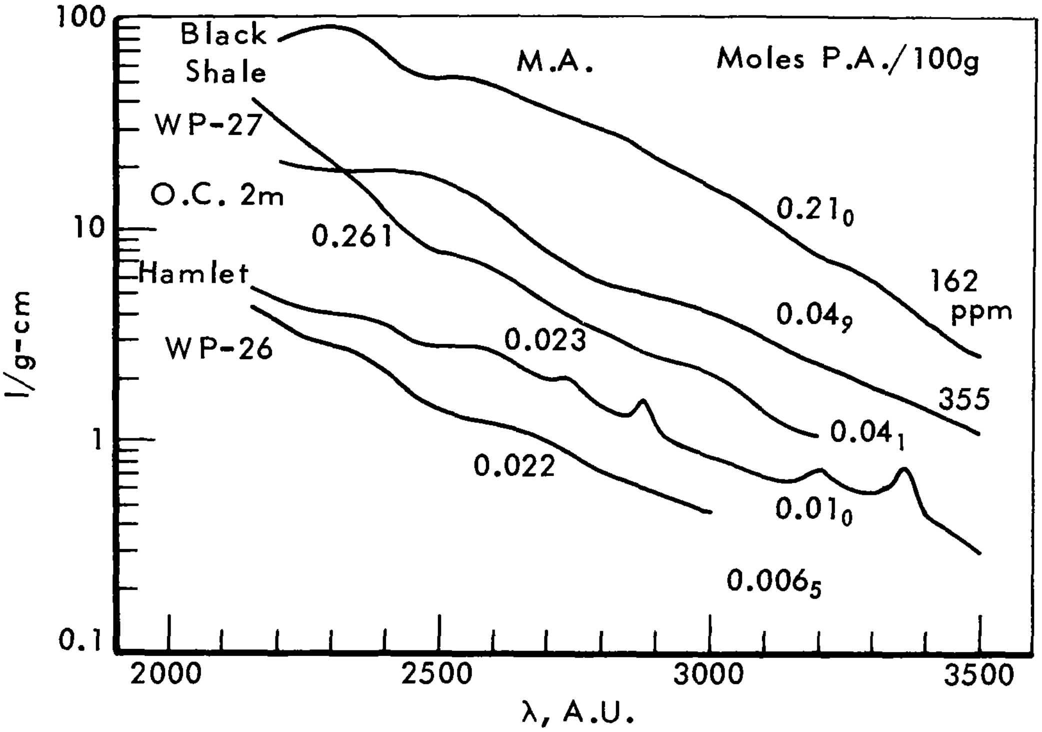

Figure 25. ULTRAVIOLET ABSORPTION SPECTRA OF THE BENZENE/ METHANOL EXTRACTS OF BLACK SHALE, KALGOORLIE SLATES WP-26 AND WP-27, 2-m OCEAN CORE SEGMENT AND THE HAMLET METEORITE SPECIMEN

It has been found that estimates of the concentration of monoaromatic nuclei[a] and polyaromatic nuclei[b] in higher molecular weight petroleum fractions may be obtained from the ultraviolet absorbance data by means of the following formulae:

$$\text{P.A.(I)} = [0.1140\, A_{2300} + 0.1205\, A_{2550} + 0.0338\, A_{2650} + 0.0585\, A_{2800}] \times 10^{-2}$$

$$\text{P.A.(II)} = [0.1309\, A_{2250} + 0.0557\, A_{2550} + 0.4290\, A_{3000}] \times 10^{-2}$$

$$\text{M.A.} = [0.909\, A_{2150}] \times 10^{-2} - 1.27\, [\text{P.A.(I)} + \text{P.A.(II)}]$$

where A_λ is the absorbance of the oil in liters/g cm at wavelength λ, and P.A. and M.A. are moles of polyaromatic and monoaromatic nuclei per 100 grams of sample, respectively. The formulae for P.A.(I) and P.A.(II) were alternate formulas devised for cases, I, where the sulfur content of the oil is low and the degree of substitution on the polyaromatic nuclei is high, and II, for cases with high sulfur content (as benzothiophene) and the degree of substitution low as in light catalytically cracked gas oils.

The results of the application of the formulae to the observed ultraviolet absorption spectra are given in Table 21. The agreement between the two estimates of the polyaromatic content of the extracts, P.A.(I) and P.A.(II) gives a measure of the reliability of the assay.

Table 21. THE AROMATICITY OF BENZENE ELUATES FROM THE CHROMATOGRAPHY OF SPECIMEN EXTRACTS

Specimen	M.A.	moles/100 grams	
		P.A.(I)	P.A.(II)
Ocean Core, 2.0-m[a]	(b)	0.046_8	0.051_6
Black Shale	(b)	0.204_3	0.217_1
Kolm	0.062	0.048_3	0.060_8
Slate WP-26	0.022	0.005_8	0.007_2
Slate WP-27	0.261	0.035_3	0.045_9
Hamlet	0.023	0.009_5	0.010_6
Chattanooga Shale	(b)	0.171_9	0.183_5

a) The benzene/methanol extract of this specimen.
b) Absorbance at 2150 A not measured.

Usable infrared spectra were obtained only of the benzene-methanol eluates from the silica gel chromatography of the extracts of the Black Shale, Chattanooga Shale and the Kalgoorlie Slate, WP-27. In addition to an undistinguished but strong band characteristic of the C-H stretch modes at 3.4-3.5 μ, these specimen showed the characteristic absorption of ester

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[a] D. P. Stevenson and H. M. McConnell, Spectrochimica Acta <u>12</u>, 262 (1958).

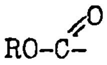
[b] R. A. Burdett, L. W. Taylor and L. C. Jones, "Molecular Spectroscopy", pp. 30-42, The Institute of Petroleum, London, 1955.

carbonyl, aromatic C-H, methylene and methyl in 5.0-8.0 μ region shown in the tracings of Figure 26. The extracts from the Black and Chattanooga Shales also showed bands characteristic of variously disubstituted benzene rings at 12.2 and 13.2 μ.

From the absorbances at 5.78, 6.83 and 7.25 μ there were estimated the concentrations (in moles/100 grams) of ester carbonyl, methylene and methyl groups as shown in Table 22. Absorptivities characteristic of these groups were taken to be:

	μ	liters/mole cm
Ester carbonyl	5.72-5.76	400
Methylene	6.8^+	15
Methyl	7.25	15

Table 22. ESTER CARBONYL, METHYLE AND METHYL CONTENT OF HETEROAROMATIC FRACTIONS OF EXTRACTS

Specimen	 $\mathrm{RO{-}\overset{\diagup O}{C}{-}}$	Moles/100 Grams	
		$>CH_2$	$-CH_3$
Black Shale	0.07_0	1.19	0.94
Chattanooga Shale	0.03_1	0.72	0.62
Slate, WP-27	0.04_6	0.76	0.72

In the case of the heteroaromatic fractions from the slate, WP-27, extract there was also estimated the total C-H (mole/grams) from the absorbance at 3.42 μ using 10 liters/mole cm as the absorptivity per C-H. This led to 3.42 moles aliphatic C-H per 100 grams in quite reasonable agreement with the weighted sum of the estimate of CH_2 and CH_3, that yields for total CH, $2 \times 0.76 + 3 \times 0.72 = 3.70$ moles/100 grams.

The low concentration of CH_2 and CH_3 per 100-gram sample indicates the condensed aromatic or heteroaromatic rings to have few, short side chains, and the low carbonyl content indicates esters to be minor constituents of the fractions.

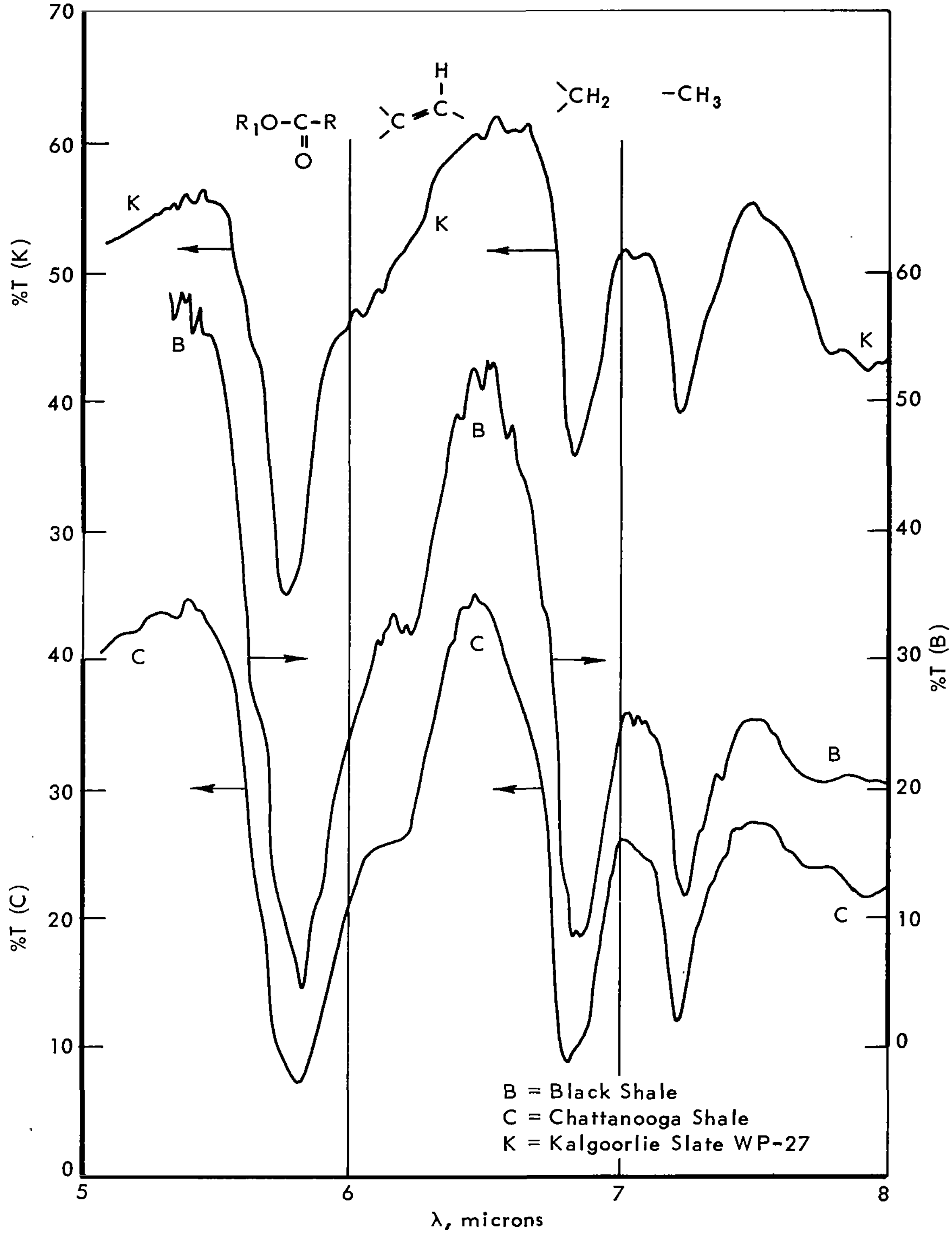


Figure 26. INFRARED SPECTRA OF THE BENZENE-METHANOL FRACTIONS OF BLACK SHALE, CHATTANOOGA SHALE AND KALGOORLIE SLATE WP-27