

CORRELATION OF HYDROCARBONS IN  
GILSONITE, TAR SAND, RED WASH CRUDE OIL  
AND OIL SHALES FROM THE GREEN RIVER  
FORMATION, UTAH AND COLORADO

by

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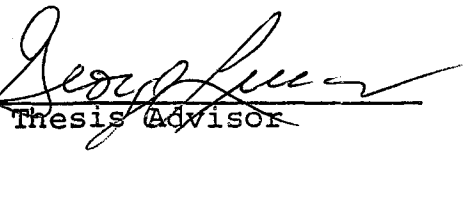
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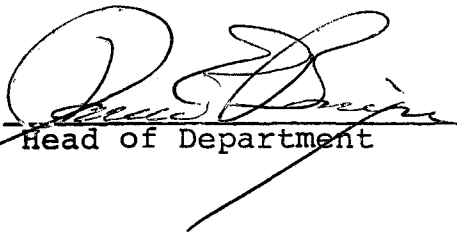
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science in Chemistry.

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ABSTRACT

Gilsonite, tar sand from Asphalt Ridge at Vernal, Utah, Red Wash crude, and oil shale from the Green River formation in Utah and Colorado were studied in an attempt to establish the source of these hydrocarbons, and possibly to find genetic relations.

The crude oil and the bitumens extracted from the above materials were subjected to liquid adsorption chromatography and gas liquid chromatographic analysis.

Similar distribution of the normal paraffin fraction, the odd to even predominance curve and similar values of the carbon preference index suggest that Gilsonite and tar sand from Asphalt Ridge originated from the same source.

A relationship found between the normal paraffin distribution of Gilsonite, tar sand from Asphalt Ridge and Red Wash crude oil indicates that Gilsonite and the tar sand probably originated from a paraffinic crude oil in the Green River formation.

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## INTRODUCTION

One of the most interesting problems in organic geochemistry is that concerned with the origin and transformation of hydrocarbons in recent and ancient sediments. The complex mixture of hydrocarbons found in these carbonaceous materials for years prevented the correlation of them with the possible organic precursors but since the development of gas chromatographic and mass spectrometric techniques, a better understanding of their composition has been possible.

Of course the existence of many geologic variables, the different processes of migration and accumulation in the reservoir and the mechanisms of reaction involved in the transformation of this organic material make the problem very complex. However, some theories have found wide acceptance within the researches of geochemistry and definite routes of genesis have been outlined.

The abiogenic (non-biologic) origin of fossil fuels has been suggested by some authors (Ponnamperuma and Pering, 1966; Ponnamperuma, 1968; Rudakov, 1967; Hodgson and Ponnamperuma, 1968) and Calvin (1969) has described the possible routes and mechanisms that account for a transition between "non-living" molecules and more complex substances called "living" molecules. However, a biogenic (biologic) origin

for most of the organic extracts of crude oils and shales is more widely accepted (Schroyer, 1968; Hills, et. al., 1968; Eglinton, et. al., 1964). Smith (1954) showed the existence of liquid hydrocarbons in recent sediments and related them to a biological origin for petroleum. Meinschein (1959) found the same kind of hydrocarbons in both the crude oils and the sediments being deposited today. Also, he showed the structural relations between the hydrocarbons found in sediments and petroleum and some of the organic compounds present in the lipid fraction of living organisms; Stevens (1956) and Meinschein (1959) reported the odd carbon preference of n-paraffins in the 23- to 35 carbon-number range in recent sediments although this predominance is not observed in most crude oils (Cooper and Bray, 1963; Martin, Winters and William, 1963). In contrast, an even-carbon-number preference for n-fatty acids has been observed in cretaceous sediments (Kvenvolden, 1966), Green River shale (Lawlor and Robinson, 1965) and in recent and ancient sediments (Cooper, 1962)

Cooper (1962) found that the odd fatty acids were more abundant in the ancient sediments than in the recent sediments indicating a conversion of even fatty acids to odd fatty acids and hydrocarbons. More recently Johnson and Calder (1973) reported that in the early diagenesis of plant produced fatty acids and hydrocarbons, in situ microbial activity appears to alter the distribution pattern of straight chain components,

to increase the branched components and to decrease the unsaturated components.

A mechanism for the conversion of n-fatty acids to n-alkanes through acyl radicals as intermediates was proposed by Cooper and Bray (1963), although they did not explain the formation of higher paraffins in the range 25- to 35-carbon number. The temperatures recorded for oil reservoirs do not exceed 220°C and probably the temperature of their source rocks have never been more than 100°C (Hedberg, 1964; Cooper and Bray, 1963). This fact suggest that the mechanisms of formation of hydrocarbons in sediments and petroleum are limited to those mechanisms possible at moderate temperatures. Shimoyama and Johns (1971), have carried out successfully the catalytic conversion of n-docasanoic acid ( $C_{21}H_{43}COOH$ ) to petroleum-like paraffins, including those with higher carbon numbers than the parent fatty acid; Waples (1972) showed the evidence of a stepwise degradation mechanism in the early reaction in the experiment of Shimoyama and Johns (1971). Jurg and Eisma (1964) suggested that the presence of water may influence the mechanism of formation of hydrocarbons obtained from the thermal degradation of n-docasanoic acid ( $C_{21}H_{43}COOH$ ) at 200°C with bentonite and that all the normal paraffins may not be derived only be decarboxylation of fatty acids with longer chain lengths.

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Sediments can be altered by three principal processes; a) bacterial degradation (Stevens, 1956; Johnson and Calder, 1973); b) radioactivity (Hedberg, 1964; Davis and Johnson, 1968); c) thermal degradation (Henderson, et. al., 1968).

Philippi (1965) has shown the role of temperature in the genesis of oil. Thermal degradation, including catalytic activation, seems to be the more accepted process for the formation of hydrocarbons in oil and sediments (Shimoyama and Johns, 1971; Waples, 1972; Philippi, 1968). The odd-to even predominance observed in recent sediments disappears with depth (Philippi, 1968; Robinson, et. al., 1965) and the predominant paraffins are shifted to lower carbon-number paraffins. The higher isoprenoid hydrocarbons decrease in content with depth and the lower-molecular-weight isoprenoid and branched hydrocarbons show a tendency to increase in content with depth (Robinson, et. al., 1965)

We may expect that some of the organic compounds of biological derivation retain enough of their structural characteristics and/or chemical properties and serve as "Biological Markers" (Anders and Robinson, 1971). Some of the "biological markers" that have been found in sediments and crude oils are:

1. Isoprenoid hydrocarbons, like pristane and phytane (Blumer and Snyder, 1965; Eglinton, etl al., 1964; Robinson, et. al., 1965; Cummins and Robinson, 1963)

- which probably are formed from the chlorophyll molecule (Krogmann, 1973).
2. Steranes, like stigmastane, ergostane, cholestane, sitostane (Anderson, et. al., 1969), triterpanes like gammacerane (Hills and Whitehead, 1966) and lupane (Burlingame, et. al., 1965). These compounds probably are derived from the phyto-steroles and pentacyclic triterpenoids (Anders and Robinson, 1971; Anderson, et. al., 1969).
  3. Pigments, or compounds derived from pigments, like  $\beta$ -perhydrocarotene (Murphy, et. al., 1967; Gallegos, 1970)
  4. Triterpenoid alcohols, like tetrahymanol, (Henderson and Steel, 1971).
  5. Normal fatty acids have been found in Green River shale by Lawlor and Robinson (1965), in Persian sediments by Welte and Ebhardt (1968) and in cretaceous sediments by Kvenvolden (1966). Eglinton, et. al., (1966) identified isoprenoid fatty acids in Green River shale.

The organic matter in sediments and oil can be associated with a marine origin or a non-marine origin. A non-marine

environment, like that found in lakes, include microorganisms like microscopic algae and non-lacustrine organic components like pollen and waxy spores (Bradley, 1970). Green algae have as high as 30% of lipids plus organic acid materials (Akiyama, 1972), and blue-green algae have normal hydrocarbons in the range n-C15 to n-C20 with n-C17 as a major components (Han, et. al., 1968). Pollen from higher plants have normal paraffins in the range C-23 to C-29 (Han, et. al., 1968; Bradley, 1970) that can be associated with the presence of higher normal paraffins in recent sediments. Souza and Nes (1968) have isolated sterols and phytane from blue-green algae. We can observe that despite the complexity of the organic material extracted from sediments and crude oil, it is possible to study their composition and to establish several correlations between them and the environment where these materials have been found, equally, we can compare the different kinds of bituminous materials found in an specific area and to associate them with a common precursor material, and possibly the diagenetic process and the factors affecting their formation, migration and accumulation can be elucidated.

The geochemical "fingerprinting" of the isoparaffin fraction has been applied with success by Albrecht and Ourisson (1969) in the study of the diagenesis of hydrocarbons of the Douala Basin, Cameroon, and by Didyk, et. al., (1972) who found strong evidence that the crude oil, Didyk has



accumulated by a secondary migration from the oil-producing strata, the Springhill formation of the Magallanes Basin of Southern Chile.

Gerrild (1972) studied an oil seep present in the Idarado mine, near Telluride, Colorado, compared it with oils from four fields in the Paradox Basin, and found a similarity between the oil from the mine and the oil from the Sierra field. Speziale (1972) made an attempt to determine the source rocks of an oil reservoir, and found that samples from the same horizon in different wells show similar distributions in the normal paraffin and branched-cyclic fractions.

In the present study a comparison of the distribution of the normal paraffins and the branched-cyclic hydrocarbons separated from bituminous materials and a crude oil from the Green River formation of Utah and Colorado is realized. The samples analyzed in this work are: Green River oil shale, Gilsonite, tar sand from Asphalt Ridge at Vernal, Utah, and Red Wash crude oil. The information obtained is used for correlation purposes, in particular to study their possible origin from the source materials in the Green River formation.

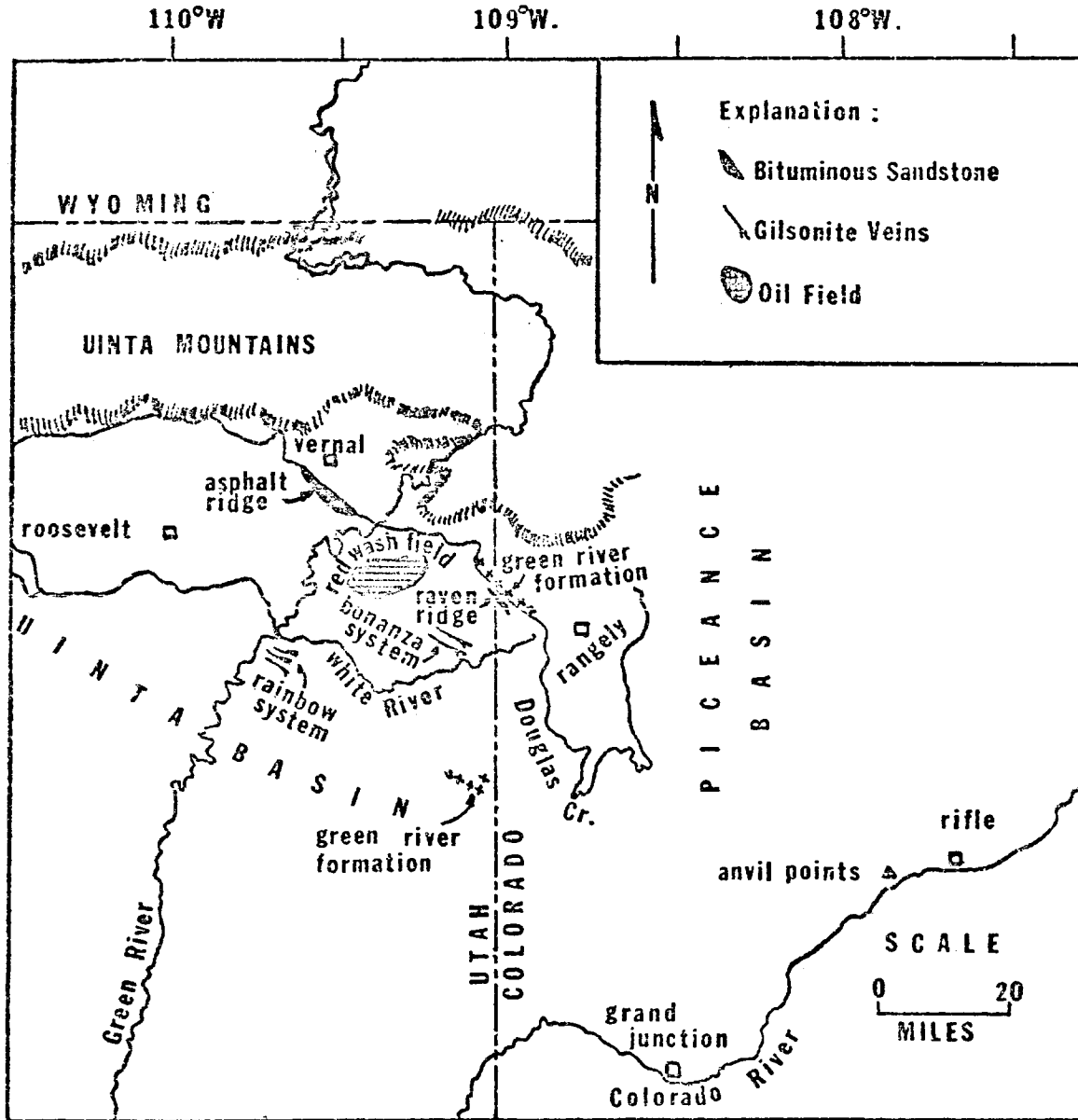


Figure 1 Index map of Uinta Basin and Piceance Basin showing location of oil and bitumens studied in this work

### Green River Formation

The Green River formation oil shale is a sedimentary rock of Eocene age (50-to 60- million years) occurring in Colorado, Utah and Wyoming (Donnell, Culberston and Cashion, 1967). The organic matter of the Green River formation was derived mainly from microscopic algae and other microorganisms and non-lacustrine organic substances like pollen and waxy spores (Bradley, 1970; Robinson, et. al., 1965) that were deposited in two lakes located in the Uinta and Piceance Basin in Utah and Colorado respectively (see figure 1)

Bradley (1970) and Han, et. al., (1968) have suggested that a class of non-marine algae, the Cyanophyceae (the blue-green algae), was the dominant precursor of the Green River oil shale. The fact that the n-C17 alkane is a predominant compound in both, the blue-green algae and the Green River oil shale, suggest an algal origin for the latter.

A series of bituminous materials as well as gas and crude oils have been found in the Uinta and Piceance Basins and together account for one of the largest reserves of hydrocarbons in the U.S.. According to Donnell, et. al., (1967) the total reserve of oil contained in the shale in the three state area is about two-trillion barrels.

### Gilsonite

Gilsonite is an asphaltite, predominately-aromatic material (Pruitt, 1961) It is a black homogeneous pitch-like

substance with a specific gravity in the range 1.05 to 1.10 and a hardness of 2.0 to 2.5 on Moh's scale (Pruitt, 1961; Cashion, 1967). Gilsonite is very brittle, it has a particular conchoidal fracture and its melting point varies in the range 250 to 400°F (Davis, 1967). According to Cashion (1967): "Gilsonite occurs as long-narrow vein deposits between the walls of north-west trending nearly vertical joints." The Cowboy vein is the largest and has a maximum width of 18 feet, a length of over 13 miles (Crawford and Pruitt, 1963) and the depth extends to as much as 1,500 feet (Cashion, 1956) The American Gilsonite Co., owned by Standard Oil Co. of California is the first privately financed company in the United States to obtain commercial petroleum products from non-petroleum sources (gilsonite) (Henderson, 1957). According to Hunt, et. al., (1957) and Davis (1957) gilsonite is derived from the bituminous materials in the Green River formation oil shales.

Solid n-paraffins in gilsonite have not been reported in the literature prior to this investigation (Hunt, 1963; Davis, 1957).

#### Bituminous Sandstones

The Uinta Basin is very rich in deposits of asphalt-impregnated sandstone. One of the richest deposits in the area is that known as Asphalt Ridge, located west and southwest of Vernal, Utah (Covington, 1957) This deposit yields

8 to 15 percent by weight of bitumen (Pruitt, 1961). The bitumen has a 12°API gravity, a low content of sulfur (0.28 wt. %) and about 1% by weight of nitrogen (Kayser, 1966). Kayser (1966) reported an unusually high content of resins (46.8% by weight), asphaltenes (19.0% by weight), oily constituents (31.6% by weight) and only a small quantity of paraffins.

The reserves in Asphalt Ridge alone can exceed two-billion barrels of crude asphaltic oil (Crawford and Pruitt, 1963). According to Covington (1957(a); 1964(b)) the source of this oil is the limestones and shales of the Green River formation.

Other deposits of bituminous sandstones exist in Peor Springs, Whiterocks Canyon, Raven Ridge and the largest known bituminous sandstone in the United States, Sunnyside in Carbon County, Utah (Covington, 1964). The hot-water separation process is more feasible on the Asphalt Ridge sandstone than on the Sunnyside sandstone.

### Green River Shale

The Green River shale has been affected little by extreme conditions of temperature, pressure, fractures, and other geological stresses (Robinson, et. al., 1965; Anders and Robinson, 1973).

The principal oil shale beds of the Green River formation are in the Parachute Creek Member, and the richest of these beds are the Mahogany Ledge and the Mahogany Zone in

the upper part of this member (Cashion, 1957).

The kerogen of the Green River shale is essentially a non-aromatic material (Robinson, 1969) that is considered to have two types of structural units: the first is the oil producing fraction, predominately aliphatic, including sulfur, nitrogen and oxygen derivatives, and the second is the carbon-residue-producing fraction (Robinson and Cook, 1971) a highly condensed aromatic structure.

Definite changes attributed to diagenesis, inorganic variations, and source variations have been observed in the Green River oil shale, and the total amount of saturated hydrocarbons increases with depth (Anders and Robinson, 1973) while the odd to even preference decreases. The alkanes seem to be generated by transformation of the non-hydrocarbon fraction of the bitumen rather than from the highly condensed kerogen (Robinson and Cook, 1971; Anders and Robinson, 1973)

#### Red Wash Crude Oil

The Red Wash field is one of the largest oil fields of Utah. It was discovered in 1951 by the California Company and according to Picard (1957) the productive zone ranges from 4.735 to 5.864 feet. The crude oil produced is dark-green to black in color with a gravity of 29 to 30<sup>o</sup>API, and a pour point of 85<sup>o</sup>F. It is classified as a paraffinic crude and it has a high content of wax.

Esthonian Shale

The Esthonian oil shale, kukersite, is a deposit of ordovician age and is considered as one of the oldest and richest in the world (430-500 million years) by some authors (Kogerman, 1931). This shale is very rich in organic material of algal origin (Duncan, 1967) and according to Kogerman and Kogwillmen (1931) it has 58.2% of organic matter. However, the amount of bitumen extracted by solvent treatment is less than 1% (Kogerman, 1931)

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## EXPERIMENTAL

### Samples

The following samples were studied under the conditions described in this research.

Sample No. 1: Oil shale from the entire Mahogany Ledge of the Parachute Creek Member of the Green River formation in the Piceance Basin, Colorado, with a particle size in the range of 0.5-2.-mm diam. This sample was donated by Dr. A. Sherrill Houghton, of the Office of Research Services, Colorado School of Mines.

Sample No. 2: Oil shale from the Mahogany Marker tuff bed of the Green River formation, taken from the Bureau of Mines experimental mine at Anvil Points, Colorado, with a particle size ranging from 2.0 to 8.0 mm diam. This sample was donated by Dr. A. Sherrill Houghton.

Sample No. 3: Green River shale sample donated by the U.S. Geological Survey and identified as sample SGR-1, split 530 by the U.S.G.S.. This sample was crushed to pass a 60-mesh screen.

Sample No. 4: Tar sand from Asphalt Ridge near Vernal, Utah. This sample was donated by Dr. A. Sherril Houghton.

Sample No. 5: Gilsonite, donated by the American Gilsonite Co. at Bonanza, Utah. This gilsonite was taken from the Cowboy-Bonanza system. The sample was crushed and then pulverized in a porcelain mortar to approximately 80-mesh.



Sample No. 6: Red wash crude oil, lighter fraction. This sample was taken from the well #15 drilled by the California Oil Co. in the Red Wash field in Utah.

Sample No. 7: Red wash crude oil, heavier fraction. This sample was also taken from the well #15 drilled by the California Oil Co. in the Red Wash field in Utah. Samples No. 6 and 7 were donated to the Chemistry Department of CSM by the University of Utah.

Sample No. 8: A sample of Esthonian Shale that has been stored at the CSM Chemistry Department for many years. It was included in this study as a matter of comparison with the Green River Shale of Colorado. The sample has a characteristic pink color and was crushed to 30-80 mesh.

#### Reagents

Normal hexane. J.T. Baker practical grade was tri-distillated, then washed with concentrate sulfuric acid until no absorption in the ultraviolet region (227-450  $\mu$ ) was observed by using a Beckman DK-2 spectrophotometer. The solvent was dried with  $\text{CaCl}_2$ , filtered and stored. Gas chromatographic analysis showed no contaminants.

Cyclohexane: Phillips 66, 98 weight % minimum was tri-distilled by using a 50 cm long column packed with glass rings, dried with  $\text{CaCl}_2$ , filtered and stored. No contaminants were found by gas chromatographic analysis.

Benzene: Mallinckrodt, spectrophotometric grade was distilled and stored.

Methanol, absolute: Mallinckrodt, analytical reagent was distilled in a 50 cm long column packed with glass rings, and used without further purification.

Phytane: (2,6,10,14 tetramethyl hexadecane) was synthesized by this worker. 10 gr of phytol, technical grade supplied by Aldrich Chemical Corp. were distilled under reduced pressure (10 mm). The distillate (9.1622 gr of phytol) was hydrogenated for 72 hours at a maximum pressure of 50 psi. in a Parr hydrogenation apparatus. The hydrogenated product was distilled under reduced pressure and 1.2191 g of phytane boiling at 170-172°C/10mm was obtained (14% of the theoretical amount). This phytane was distilled under vacuum (169.5/9.5 mm) and 1.1905 g was obtained (13.6% of the theoretical amount) Chromatographic analysis showed a purity >98%.

Pristane: practical grade, supplied by Eastman Organic Chemicals was distilled twice under reduced pressure.

Normal Hydrocarbons: Decane (C-10), dodecane (C-12), tetradecane (C-14), hexadecane (C-16), octadecane, eicosane (C-20), docosane (C-22), tetracosane (C-24), octacosane (C-28), dotriacontane (C-32) and hexatriacontane (C-36) chromatographic grade were supplied by Applied Science Laboratories, Inc.

Squalene: (C<sub>30</sub>H<sub>50</sub>), chromatographic grade, from Analabs was used as standard.

Silica Gel: Davison grade 923, 100-200 mesh size activated as it is explained in the gas-liquid chromatography section.

Molecular Sieve Linde 5A in the form of 1/16" pellets.

### Extraction

The bitumen or soluble organic matter was extracted from 10 to 20 g of sample placed in a Soxhlet extractor. One hundred and fifty milliliters of normal hexane was used for the extraction. The sample was treated during 72 hours in order to extract the maximum amount of organic matter, then the solution was concentrated in a Rhinco roto-evaporator using a Cenco Hivac vacuum pump. The temperature of the water bath used for concentrating the solution was kept within 40 to 45°C in order to avoid the loss of volatile fractions.

The concentrated solution was poured in weighed 5 ml screw-cap vials and dried further with nitrogen to constant weight until the difference between successive weights of the vials was less than 0.5 mg. The yield of bitumen extracted from each of the samples is shown in Table I.

### Liquid-Adsorption Chromatography

The separation of the saturated hydrocarbons, the aromatic hydrocarbons and the asphaltic or more polar fraction was realized by using a chromatographic technique previously described by Fergusson (1962)

TABLE I

Yield of Bitumen Obtained by Extraction With  
Normal Hexane, 48 Hours

<u>Sample</u>	<u>Yield, Wt %</u>
Entire Mahogany Ledge - Parachute Creek, Green River Formation	1.48
Mahogany Marker - Green River Formation, Anvil Points Mine, Rifle, Colorado	5.07
Green River Shale, SGR - 1, USGS	2.45
Gilsonite from the Cowboy-Bonanza System at Bonanza, Utah	39.78
Tar Sand from Asphalt Ridge, Vernal, Utah	13.89
Esthonian Shale, from Esthonia	0.14

A glass column with 15 mm ID and 70 cm length was packed with 100-200 mesh Davison Code 923 silica gel. A slurry of silica gel was formed with normal hexane and then it was added to the top of the column. For the analysis of the bitumens extracted from gilsonite and tar sand from Asphalt Ridge, Vernal, Utah, longer columns were required (110 cm length) and the sample to adsorbent ratio was about 1/820. Sample to adsorbent ratios in the range 1/450 to 1/550 were required for the rest of the samples. The silica gel was pretreated by boiling a slurry of the gel in concentrated nitric acid for two hours. The acid was separated by decantation and the silica was washed 12 times with deionized water. The silica gel was activated by heating at 275°C in a dry oven for 48 hours. The activated gel was kept under vacuum in a desiccator.

One hundred to two hundred mg of sample was dissolved in 5 ml of normal hexane and this solution was added to the top of the column. The saturated hydrocarbons were eluted with 125 ml of normal hexane added in 5 ml portions to maintain a constant liquid level on the column thus avoiding the formation of air bubbles or channels which produce a loss of efficiency. The saturated hydrocarbons eluted with normal hexane were collected in 15 test tubes and each of these fractions were analyzed in the ultra-violet region between 226 to 400 m $\mu$  in a model DK-2 Beckman spectrophotometer. No absorption was observed in any of these fractions,

showing the absence of aromatic compounds. All the fractions collected in the test tubes were mixed forming a total saturated hydrocarbon fraction.

The so called aromatic fraction was eluted with 125 ml of benzene added in 5 ml portions. When a change in coloration produced by the aromatic compounds was observed in the eluant, the aromatic fraction receiver was installed at the bottom of the column.

Next, the asphaltic or more polar compounds were eluted with 125 ml of a 50 percent benzene-methanol mixture added in 5 ml portions. The characteristic dark-brown color of the asphaltic fraction was a guide to changing the flask at the bottom of the column used for collecting the eluants.

The saturated hydrocarbon fraction, the aromatic fraction and the asphaltic fraction were concentrated in a Rhinco roto-evaporator, transferred to weighed screw-cap vials and dried further with nitrogen to constant weight until the difference between successive weighing was less than 0.5 mg. The weights of each fraction in each of the samples is shown in Table II.

#### Gas-Liquid Chromatography

The saturated hydrocarbon fraction of each of the samples was subjected to gas-liquid chromatography analysis using a Beckman GC-5 gas chromatograph at the Department of Chemistry

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TABLE II

## Liquid Adsorption Chromatography on Silica Gel

<u>Name</u>	<u>Total Wt%</u> <u>Paraffins</u>	<u>Total Wt%</u> <u>Aromatics</u>	<u>Total</u> <u>Asphaltenes</u>
Entire Mahogany Ledge Parachute Creek	14.9	29.6	55.5
Mahogany Marker, Anvil Points, Rifle, Colo.	19.6	22.6	57.8
Green River Shale SGR-1, USGS	20.8	22.1	57.1
Gilsonite	8.9	39.2	51.9
Tar Sand, Asphalt Ridge, Vernal, Utah	7.7	42.5	49.8
Red Wash Crude Oil Heavier Fraction	58.6	33.1	8.3
Red Wash Crude Oil Lighter Fraction	61.9	30.8	7.2

NOTE: Esthonian oil shale is not included in this table because of the loss caused by volatilization of the hydrocarbons.

of the Colorado School of Mines. Standard solutions of some isoprenoid hydrocarbons, pristane (2,6,10,14-tetramethylpentadecane), phytane (2,6,10,14-tetramethylhexadecane) and squalene ( $C_{30}H_{50}$ ) were used in order to identify these important biological markers (Streibl and Herout, 1969). Standard solutions of normal paraffins were used in identifying the carbon number of these hydrocarbons. Other cyclic and branched hydrocarbons can be identified from the work done by many researchers that used combined gas chromatography and mass spectrometry for the study of Green River Shale hydrocarbons. The chromatogram of the total hydrocarbon fraction of each sample are included in the appendix I.

The chromatographic column and the operating conditions of the gas chromatograph are explained at the end of the experimental part in the section named, "Operating Conditions of the Gas Chromatograph."

#### Separation of Normal Paraffins

The separation of the normal paraffins from the branched cyclic hydrocarbons was realized by using molecular sieves. This technique was first described by O'Connor, et. al., (1962) and the method has been modified by Brunnock (1966) and Fabre, et. al., (1968)

The total saturated hydrocarbon fraction was dissolved in 5 ml of cyclohexane and then was placed in a 25 ml



Erlenmeyer flask equipped with ground glass stopper. Then, 1/16 in. pellets of Linde 5A<sup>0</sup> molecular sieve were added quickly to this solution, and an additional amount of cyclohexane necessary to cover the pellets was added. The amount of molecular sieve used was about 200 mg for each mg of total saturated hydrocarbon fraction. The flask was closed with the glass stopper and the sample was left with the sieve for 120 hours at room temperature. The sieve had been previously activated for 48 hours at 330<sup>0</sup>C while purging with dry nitrogen.

Next, the cyclohexane solution containing the branched and cyclic hydrocarbons was separated from the sieves by filtering with pure white semicreped Sargent filter paper and washing twice with hot cyclohexane. The sieve pellets were transferred to a Soxhlet extraction apparatus and extracted with benzene for 24 hours in order to remove the branched and cyclic hydrocarbons absorbed from the surface of the sieves. This benzene was added to the cyclohexane solution, forming a total branched cyclic hydrocarbon solution that was concentrated in a Rhinco roto-evaporator, transferred to previously weighed screw-cap vials and dried further with nitrogen until the difference between successive weighings was less than 0.5 mg. The results are in Table III.

The sieve pellets were transferred to Teflon beakers, covered with benzene and then dissolved by adding 48% hydrofluoric acid. The benzene fraction containing the normal

TABLE III

Analysis of Paraffinic Fraction (Total) - Separation by Molecular Sieve 5A<sup>o</sup>

Name	Number	Wt. mg.		Wt. mg.		Wt. mg.		Branched Paraffins Δ%
		Total Paraffins	Normal Paraffins	Normal Paraffins	Branched+ Cyclic Paraffins	% Normal Paraffins	% Branched Paraffins	
Entire Mahogany Ledge Parachute Cr.	1	29.4	4.3	4.3	25.0	14.7	85.3	0.34
Mahogany Marker (Rifle Mine, Anvil Points, CO.)	2	28.6	5.1	5.1	23.5	17.8	82.2	0.00
Green River Shale SGR-1 USGS	3	30.4	4.6	4.6	23.8	16.2	83.8	7.00
Gilsonite (Cowboy Vein Am. Gilsonite Company)	4	16.1	1.3	1.3	14.8	8.1	91.9	0.00
Tar Sand Asphalt Ridge (Vernal, UT)	5	33.9	1.1	1.1	31.3	3.4	96.6	4.6
Red Wash Crude (Lighter fraction)	6	45.4	15.2	15.2	29.4	35.0	65.0	1.8
Red Wash Crude (Heavier Fraction)	7	37.8	12.7	12.7	25.0	33.7	66.3	.2
Esthonian Shale	8	15.1	6.1	6.1	8.9	40.7	59.3	.7

paraffins was separated by decantation, concentrated in a Rhinco roto-evaporator, transferred to previously weighed screw-cap vials and dried further with nitrogen to constant weight. The weights of the normal paraffins of each sample are in Table III.

A first attempt to separate the normal paraffins from the branched cyclic hydrocarbons failed because the extraction of the sieves with benzene in the Soxhlet extractor was omitted and the sieves were only washed twice with hot cyclohexane.

The fact that the refluxing of the sieves with benzene for 24 hours gives better separation of the normal paraffins indicates that effectively some branched and cyclic hydrocarbons are absorbed on the surface of the sieves. This effect explains the presence of branched cyclic paraffins in the normal paraffins fraction that has been attributed to occur as a consequence of too long periods of activation of the sieves by Speziale (1972) or too short periods of activation by Gerrild (1972).

In general, a better separation of the normal paraffins is realized by following the steps described below:

1. Activation of 1/16 in. pellets of molecular sieve 5A at 330°C for 48 hours, while purging with dry nitrogen then kept the sieve under vacuum.

2. Leave the total saturated hydrocarbons in contact with the molecular sieve 5A pellets for 120 hours. Use as solvent cyclohexane or benzene just covering the sieves.
3. Filter the solvent solution (cyclohexane or benzene) on filter paper and wash the sieves three times with hot cyclohexane (or benzene).
4. Transfer the sieve pellets to a Soxhlet extraction apparatus and extract with benzene for 48 hours in order to remove the branched cyclic hydrocarbons absorbed on the sieves.
5. Add the solvent from the Soxhlet extractor to the solvent from the filtration in No. 4, and concentrate this solution (it contains the branched-cyclic hydrocarbons)
6. Dissolve the sieve pellets in a teflon beaker with HF (48%) mixed with a solvent (cyclohexane) Transfer this solvent (cyclohexane) with the normal paraffins to a flask and concentrate.

The normal paraffins fraction and the branched cyclic hydrocarbons fraction of each of the samples were dissolved in 1 ml of cyclohexane and then they were analyzed in a Beckman GC-5 gas chromatograph at the Colorado School of Mines.

Standard solutions of different concentrations of normal paraffins were prepared in cyclohexane. Similar standard solutions of phytane, pristane and squalene were also prepared.

Standard curves for each of the hydrocarbons included in the standard solutions were made by plotting the area obtained by the triangulation method (McNair and Bonelli, 1969) versus the concentration in ppm. The concentration of each hydrocarbon in the samples was calculated by injecting a volume of sample solution equal to the volume of standard solution injected for the calculation of the respective standard curves. The area of the peaks in the chromatograms obtained from the samples was calculated by triangulation and the concentration was found from the standard curves. The identification of the hydrocarbons in the samples was carried out by comparison of the retention times with the standards and also by addition of an internal standard to a volume of sample.

Some of the normal paraffins analyzed were not present in the standard solutions and they were calculated by using the relative response factors reported by Spears, et. al., (1963) and included in Table IV. The relative response factors of some of the higher normal paraffins were calculated by interpolation from the values reported by Pears (1963) as is indicated in Table IV.

TABLE IV

<sup>1</sup> Relative Response Factors of Normal Alkanes With  
FID<sup>2</sup> Detectors

<u>Carbon No.</u>	<u>Relative Response (Area/Unit Wt.)</u>
10	1.79
11	1.75
12	1.70
13	1.66
14	1.61
15	1.57
16	1.53
17	1.49
18	1.44
19	1.41
20	1.38
21	1.35
22	1.31
23	1.27
24	1.24
25	1.21
26	1.18
27	1.15
28	1.12
29	1.10
30	1.07
31	1.04
32	1.02
33	1.00
34	.98 *
35	.96 *
36	.94 *

1) Data taken from Spears (1963)

2) Flame Ionization Detector

\* Calculated by Interpolation

The following equation was used in order to calculate the concentration of the normal paraffins not included in the standard solutions:

$$A_{CS} = \frac{A_x}{F_x} \times fcs$$

where,

$A_x$  = Area of the normal paraffin in the sample to be calculated and not included in the standards solutions.

$F_x$  = Relative response factor of the normal paraffin in the sample to be calculated and not included in the standards solutions.

$A_{CS}$  = Converted area of the normal paraffin in the sample, which concentration is calculated from the standard curve of the normal paraffin with relative response factor  $fcs$ .

The chromatograms of the normal paraffins and branched plus cyclic hydrocarbons are presented in the Appendix I.

Operating conditions of the gas chromatograph. The gas liquid chromatographic analysis reported in this work were done in a Beckman GC-5 gas chromatograph operated under Linear Temperature Programming Gas Chromatography (LTPGC) conditions. After the injection of sample, the temperature was constant at 100°C for one minute, then linearly increased to 300°C in 32 minutes and the analysis ended when no more compounds were eluted.

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The chromatograph was equipped with two matched 6 feet long, 1/8 in. ID columns packed with 3% Se-30 on 100-120 mesh Chromosorb-W (high performance, acid washed).

A flame ionization detector was used with helium gas carrier flow of 40 cc/min at 80 psig. The hydrogen flow was 40 cc/min, and the air flow was 275 cc/min.

The speed of the chart was 0.5 in/min and the amount of sample analyzed was about 0.05 mg.



## DISCUSSION OF RESULTS

The results of the liquid adsorption chromatography and gas liquid chromatography analysis are discussed below.

### Liquid Adsorption Chromatography

The bitumens extracted from the Entire Mahogany Ledge, Mahogany Marker and Green River shale SGR-1 have similar percentages of saturated hydrocarbons, aromatic hydrocarbons and more polar compounds (asphaltenes), with the latter representing the larger fraction (see Table II).

The bitumens extracted from Gilsonite and the tar sand from Asphalt Ridge have similar percentages of saturated hydrocarbons, aromatic hydrocarbons and more polar compounds (alsphaltenes). These two bitumens have a lower percentage of total saturated hydrocarbons and a higher percentage of aromatic hydrocarbons than the bitumens from the Green River oil shales (Table II).

The Red Wash crude oil is a very paraffinic crude with about 60% of the total being saturated hydrocarbons and a low content of more polar compounds (asphaltenes). The heavier fraction of this crude oil has a higher content of aromatic hydrocarbons and polar compounds than the lighter fraction (see Table II).

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The relative percentage of normal paraffins and branched cyclic paraffins in the total saturated hydrocarbons fraction are included in Table III. The three samples from the Green River oil shales have similar values.

Gilsonite and the tar sand from Asphalt Ridge form a second group with the highest relative percentage of branched cyclic hydrocarbons (see Table III). Gilsonite has a larger relative percentage of normal paraffins than the tar sand.

The Red Wash crude has the highest relative percentage of normal paraffins of all of the samples.

The Esthonian oil shale will not be considered for our discussion and the data are given only as a matter of information about this old oil shale.

### Gas Liquid Chromatography

#### Normal Paraffins

The normal paraffins distribution of the Green River oil shale samples (Entire Mahogany Ledge, Mahogany Marker, and Green River shale SGR-1) are very similar. The maximum relative percentage is found at n-29 for Entire Mahogany Ledge and Green River shale SGR-1 while the Mahogany Marker has n-C31 as the predominant normal paraffin (see Table V). The odd to even predominance values (O.E.P.) were calculated by using the method given by Scalan and Smith (1970). The O.E.P. curves for this group of Green River oil shale samples

TABLE V

Relative Weight Per Cent Distribution of Normal  
Paraffins in Oil Shales Studied in This Work

Sample	Entire Mahogany	Mahogany Marker	Green River Shale SGR-1	Esthonian Shale
Carbon No.	% Wt. (Relative)	% Wt. (Relative)	% Wt. (Relative)	% Wt. (Relative)
12				.63
13				9.87
14				15.18
15	.28	.56	1.52	11.91
16	1.24	.60	1.55	7.73
17	7.55	5.29	8.40	7.26
18	2.09	.81	2.67	4.52
19	3.21	1.53	3.42	5.47
20	2.69	1.27	2.47	4.65
21	3.33	2.26	4.58	5.91
22	6.46	3.60	7.33	4.62
23	5.58	4.22	6.62	5.88
24	5.58	3.39	4.74	3.30
25	6.30	6.74	8.70	3.74
26	5.30	4.20	4.08	1.85
27	7.64	7.41	7.97	1.57
28	5.22	4.23	3.42	1.24
29	11.25	16.60	11.27	1.16
30	4.38	4.13	2.47	.69
31	10.85	19.07	10.68	1.07
32	2.95	2.86	1.50	.47
33	4.82	8.09	5.04	.69
34	1.20	1.08	.53	.28
35	.88	1.13	.58	.31
36	.48	.33	.23	
37	.44	.39	.23	
38	.28	.21		

The error limits of these data is 10%.

TABLE VI

Relative Weight Percent Distribution of Normal  
Paraffins in Gilsonite, Tar Sand (Asphalt Ridge)  
and Red Wash Crude Oil

Sample	Gilsonite	Tar Sand (Asphalt Ridge)	Red Wash Crude Lighter Fraction	Red Wash Crude Heavier Fraction
Carbon No.	% Wt. (Relative)	% Wt. (Relative)	% Wt. (Relative)	% Wt. (Relative)
12			.85	
13			1.23	.80
14			2.44	1.96
15	.21	.38	2.68	2.49
16	.24	.53	3.90	3.64
17	2.23	3.08	4.35	4.44
18	1.47	1.24	4.53	4.54
19	.93	1.20	4.55	4.81
20	1.30	1.52	4.71	4.90
21	3.21	3.50	5.40	5.13
22	8.15	8.99	5.88	6.13
23	11.89	12.16	6.78	6.40
24	12.55	12.35	6.66	6.53
25	12.63	12.92	7.29	7.26
26	10.27	10.45	6.09	6.04
27	8.48	8.55	6.18	6.34
28	5.70	5.70	5.31	5.57
29	4.89	4.47	4.67	5.14
30	3.89	2.94	3.79	3.73
31	3.89	3.13	3.40	3.84
32	2.36	1.80	2.84	2.94
33	2.28	1.90	2.12	2.51
34	1.30	1.23	1.44	1.58
35	.90	.76	1.03	1.17
36	.82	.72	.81	.87
37	.41	.48	.59	.66
38			.47	.58

The error limits of these data is 10%.

TABLE VII  
O.E.P. Values for the Samples Studied

Sample No.	1	2	3	4	5	6	7	8
Carbon No.	O.E.P	O.E.P	O.E.P.	O.E.P.	O.E.P.	O.E.P.	O.E.P.	O.E.P.
14						.81		.88
15						.85	.90	.97
16						.92	.98	1.16
17	3.66	6.00	3.28	2.83	2.12	.99	1.04	1.24
18	2.61	4.05	2.36	1.80	1.22	.99	1.03	1.29
19	1.58	2.01	1.63	1.25	.99	1.00	1.02	1.25
20	1.06	1.26	1.29	.97	.95	1.03	.95	1.23
21	.79	.99	.96	.82	.85	1.03	.95	1.26
22	.76	.99	.88	.92	.96	1.04	.96	1.32
23	.90	1.23	1.10	1.05	1.05	1.06	1.00	1.42
24	1.05	1.56	1.54	1.07	1.05	1.08	1.06	1.46
25	1.17	1.71	1.89	1.08	1.05	1.11	1.12	1.45
26	1.31	1.72	2.04	1.02	1.06	1.11	1.13	1.36
27	1.51	2.01	2.26	1.06	1.07	1.07	1.09	1.16
28	1.84	2.85	2.84	1.09	1.11	1.04	1.06	1.09
29	2.24	3.77	3.66	1.11	1.09	1.03	1.10	1.24
30	2.57	4.48	4.45	1.21	1.12	1.04	1.16	1.52
31	2.77	4.98	5.06	1.33	1.22	1.02	1.16	1.78
32	2.69	4.86	5.24	1.34	1.28	.99	1.11	1.86
33	2.45	4.36	5.11	1.26	1.26	1.00	1.11	1.84
34	2.14	3.81	4.58	1.07	1.16	1.02	1.11	
35	1.57	2.70	2.88	.89	.95	.99	1.04	
36	1.21	1.86				.96	.99	

The error limits of these data is 10%.

TABLE VIII

Carbon Preference Index (C.P.I.) in the  
n-C25 to n-C33 Range

<u>Sample No.</u>	<u>Sample Name</u>	<u>C.P.I.</u>
1	Entire Mahogany Ledge	1.94
2	Mahogany Marker	3.30
3	Green River Shale SGR-1 (U.S.G.S.)	3.17
4	Tar Sand (Asphalt Ridge)	1.17
5	Gilsonite	1.15
6	Red Wash crude, lighter	1.09
7	Red Wash crude, heavier	1.14
8	Esthonian shale	1.45

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follow a similar pattern (Fig. 2) with values higher than 2.0 and a characteristic maximum at n-C31. The carbon preference index (C.P.I.) was calculated by using the method given by Cooper and Bray (1963). The C.P.I. values for this group are higher than those found for the other bitumens and crude oil from the Green River formation (see Table VIII). The normal paraffins of the Green River oil shale follow a bimodal distribution with a first maximum in n-C17 and a second maximum in n-C29 or n-C31 (see Figs. 14, 15, and 16, Appendix I).

Gilsonite and the tar sand from Asphalt Ridge have very similar paraffin distribution (Table VI; Figs. 17 and 18, Appendix I). The predominant hydrocarbon in the distribution of normal paraffins of gilsonite, tar sand (Asphalt Ridge) and Red Wash crude is n-C25 (Table VI; Figs. 12, 13, 17 and 18, Appendix I). The O.E.P. curves for this group are very similar in the range 19-to 36-normal-paraffin carbon-number (see Fig. 3 and Table VII). The C.P.I. values of gilsonite, tar sand (Asphalt Ridge) and Red Wash crude oils have C.P.I. values of 1.0 and the maximum reported is about 1.15 (Koons, Jamieson and Cierezko, 1965). Ancient sediments have C.P.I. values somewhat higher than crude oils (Cooper and Bray, 1963). The Red Wash crude contains more smaller normal paraffins than gilsonite and the tar sand from Asphalt Ridge.

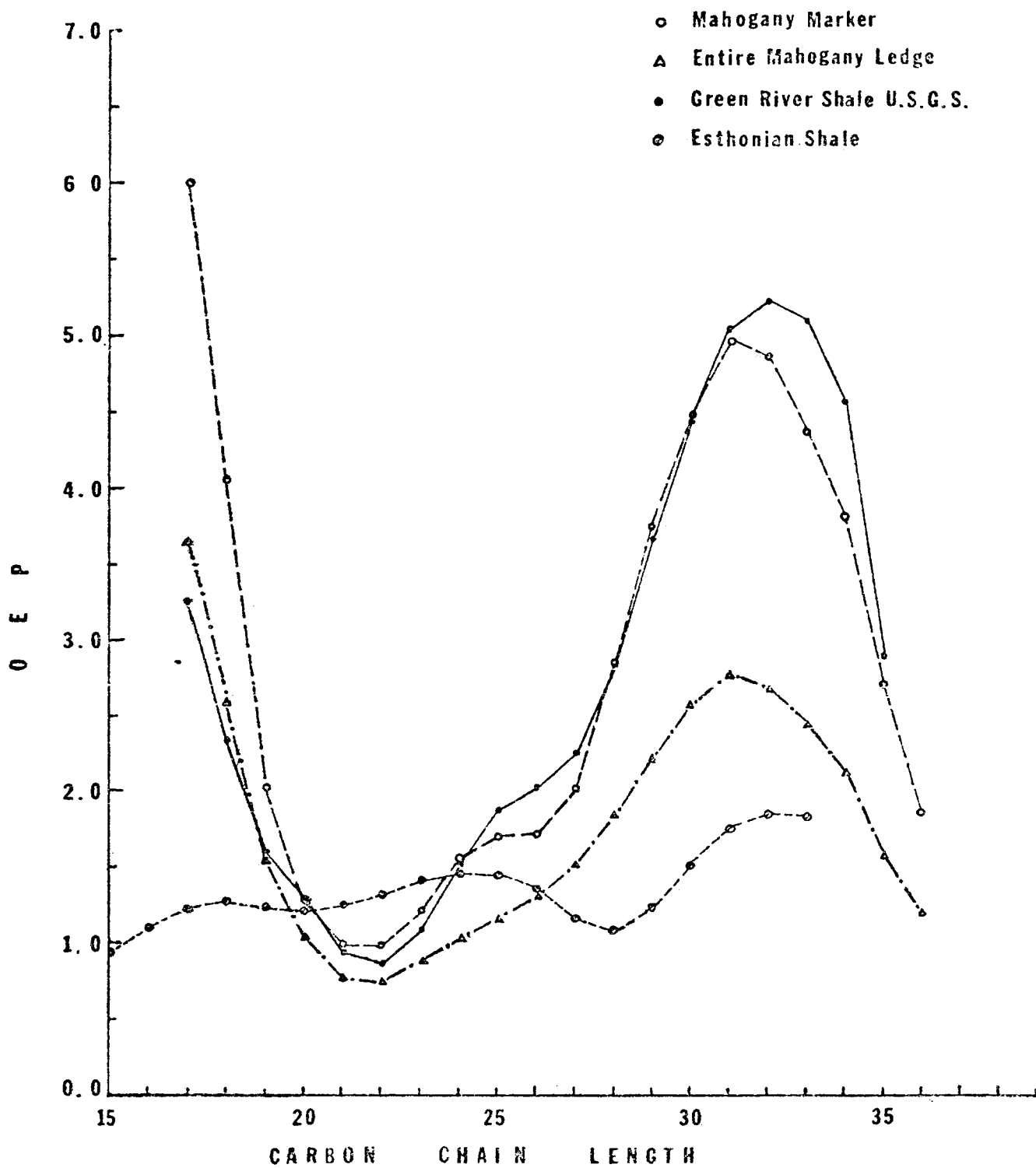


Figure 2 GEP curves for Green River oil shales and Esthonian oil shale



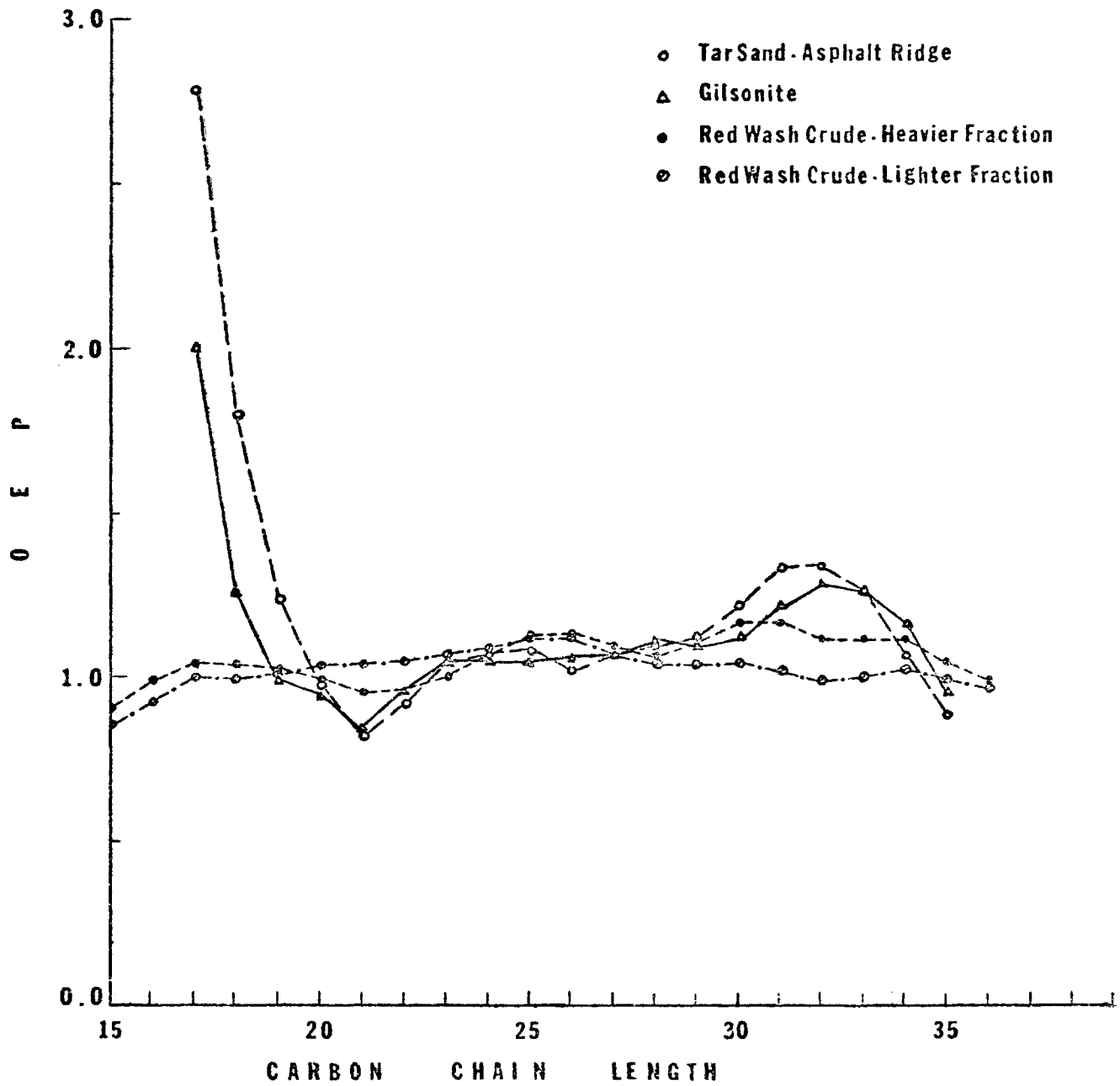


Figure 3 OEP curves for Red Wash crude oil, gilsonite and tar sand.

From the above analysis it is logical to recognize that there is an important correlation in the normal paraffins distribution of gilsonite, tar sand and Red Wash crude oil. This fact suggests a common origin at least for the normal paraffin fractions of these organic materials. Previous workers have explained that gilsonite (Pruitt, 1961; Davis, 1957) originated in the Green River formation and that the original hydrocarbon type substances migrated upward into the fractures where it is found. Although Davis (1957) suggests that gilsonite is a product of reaction and conversion rather than a product of evaporation, Pruitt (1961) accepts that many of the volatiles have been lost. The asphalt associated with tar sands (like Asphalt Ridge) seems to be originated from the oil of the lower Green River formation which migrated updip along the unconformities in the Asphalt Ridge structure (Kayers, 1966; Covington, 1957). According to Picard (1957) most of the Red Wash crude oil wells produce from the Douglas Creek Member, and the middle and upper parts of the Garden Gulch Members of the Green River formation.

Because the normal paraffins are quite stable with respect to cracking in this complex mixture of compounds, it is very important to recognize, that we should expect to find a closer relationship between the distribution of normal paraffins of gilsonite and tar sand (Asphalt Ridge) and the distribution of normal paraffins of the Green River oil shales if both

gilsonite and tar sand were formed from the Green River oil shale. Instead, we find many differences such as the loss of the odd to even predominance in the former group and the absence of the strong predominance of n-C31, n-C29, and n-C17 in gilsonite and tar sand from Asphalt Ridge.

These facts suggest that both gilsonite and the tar sand (Asphalt Ridge) come from a) a source of hydrocarbons more mature than the Green River oil shale or b) they were exposed to diagenetic processes such as high temperature and pressure during or after the migration. This last possibility seems to be unlikely since the composition of the sediments (Green River oil shale) is unchanged in the area around the gilsonite veins or the asphalt deposits.

The absence of the lower normal paraffins in gilsonite and tar sand (Asphalt Ridge) can be a result of the alteration by water washings. This "water washings" affects more the lighter hydrocarbons (more soluble) than the heavier normal paraffins (Bailey, et. al., 1973).

#### Branched Cyclic Hydrocarbons

The branched paraffins distribution of the Green River oil shale samples have a characteristic appearance. The phytane to pristane ratios of this group of samples are higher than 2.0. Phytane and steranes are major components of the Entire Mahogany Ledge and Green River shale SGR-1,

while the Mahogany Marker shows a high predominance of phytane and  $\beta$ -perhydrocarotene. C-18 and C-16 isoprenoids are characteristic of these three samples (see Figs. 22, 23 and 24).

Gilsonite and Red Wash crude oil have phytane to pristane ratios close to 1.0, with a value of 1.17 and 0.92 respectively (see Table IX). The tar sand (Asphalt Ridge) does not show any peak corresponding to phytane or pristane.

Gilsonite shows an unusual predominance of  $\beta$ -perhydro carotene. However, this compound is absent in the tar sand (Asphalt Ridge) (see Figs. 25 and 26, Appendix I).

Red Wash crude oil shows a predominance of C-16, C-18, C-19 (pristane) and C-20 (phytane) isoprenoids and lower molecular weight hydrocarbons.  $\beta$ -perhydro carotene is present in Red Wash crude and it is a slightly predominant hydrocarbon at the end of the chromatogram. Steranes are probably present but are not predominant components.

The absence of phytane, pristane and  $\beta$ -perhydro carotene in tar sand can be related to; a) a selective adsorption of these compounds or their precursors during the migration of the original organic matter, or b) lost by solubilization in water, or c) these components were not present in the original bitumen. In this latter possibility, gilsonite may have gotten these hydrocarbons as "contaminants" during its migration. However, the distribution of hydro-

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TABLE IX

## Phytane to Pristane Ratio

<u>Sample</u>	<u>Ratio</u> <u>(Phytane:Pristane)</u>
Entire Mahogany - Ledge, Parachute Creek	2.19
Mahogany Marker - (Green River Formation, Anvil Points, Colo.)	2.42
Green River Shale, SGR-1 U.S.G.S.	3.19
Gilsonite - (Cowboy Vein, American Gilsonite Co.)	1.17
Asphalt Ridge (Vernal, Utah)	(a)
Red Wash Crude (Lighter)	.92
Red Wash Crude (Heavier)	.91

(a) Phytane and pristane absent.

carbons in the steranes group is very similar for both Gilsonite and tar sand (Asphalt Ridge).

### CONCLUSIONS

From the liquid adsorption chromatography and gas liquid chromatography analysis the following facts are evident:

1. The normal paraffin distribution of Gilsonite and tar sand from Asphalt Ridge (Vernal, Utah) are almost identical.
2. The normal paraffin distribution of Gilsonite, tar sand from Asphalt Ridge and Red Wash crude oil have as the predominant compound the normal paraffin with 25 carbon number.
3. The O.E.P. curves and C.P.I. values for the normal paraffin distribution of Gilsonite, tar sand (Asphalt Ridge) and Red Wash crude oil are very similar and close to 1.0 indicating a correlation between these carbonaceous materials as well as similar levels of maturation.
4. The liquid adsorption chromatography analyses show a similar composition of the bitumens extracted from Gilsonite and tar sand (Asphalt Ridge)
5. The relative composition of the saturated fraction of Gilsonite resembles more that of the tar sand, and the

the relative compositions of the saturated fraction of these two is different from that of the Green River oil shales.

These similarities found between the composition of the normal paraffin fraction of Gilsonite and tar sand from Asphalt Ridge strongly suggest that these two bituminous materials were originally from the same source.

The relationship found between the normal paraffin distribution of Gilsonite, tar sand from Asphalt Ridge and Red Wash crude oil makes acceptable the idea that Gilsonite and tar sand probably originated from crude oil in the Green River shale formation that migrated updip filling the cavities and fractures where those bitumens are found today. Different processes of maturation, temperature, solubility in water, and catalysis by the inorganic minerals have affected the less stable compounds.

The Green River oil shale seems to be less affected by those factors mentioned above because we can observe clearly an odd to even predominance with strong maximums at the 31, 29 and 17 carbon number paraffins, indicating that these oil shales have not matured as much as the Red Wash, Gilsonite or tar sand from Asphalt Ridge.



### FUTURE WORK

The present work is a contribution to the study of the composition and origin of the bitumens and oils found in the Green River formation of Utah and Colorado.

More research has to be realized in order to get more information about the composition and diagenesis of these valuable carbonaceous materials. Some of the fields of work where further investigation can be oriented to get support for the conclusions given in this thesis are outlined below.

1. Study of the aromatic fraction of these organic materials by gas chromatography and mass spectrometry. The work done by Anders, et. al., (1973) show that the aromatic fraction of Green River shale has some very predominant hydrocarbons. Preliminary gas chromatography analysis carried out by this worker at the Chemistry Department of the Colorado School of Mines indicates that the distribution of aromatic hydrocarbons, in the bitumens studied in this work can give more information about their genetic relationships despite the thermal instability attributed to aromatic hydrocarbons.
2. Carbon isotopic composition of the saturated hydrocarbons, aromatic hydrocarbon and more polar (or asphaltenes) fractions separated from these bitumens and oils are very

important in order to get more information about their origin and migration, as has been explained by Silverman and Epstein (1958). However, better results can be obtained by studying the carbon isotopic composition of specific hydrocarbons separated from the bitumens and oils, especially those predominants known as "biological markers", such as phytane, pristane, steranes,  $\beta$ -perhydrocarotene, and those predominant aromatics like the carotenoids with aromatic end groups.

3. Sulfur isotopic composition of the asphaltenes or more polar fraction of these carbonaceous materials should be obtained in order to establish more genetic correlations.
4. Samples of Gilsonite and tar sand from Asphalt Ridge, taken from different depths have to be studied in order to establish their variations with depth, temperature, and mineral environment. These samples have to be compared with samples of Green River oil shale taken from the same stratigraphic level.

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APPENDIX I  
Chromatograms

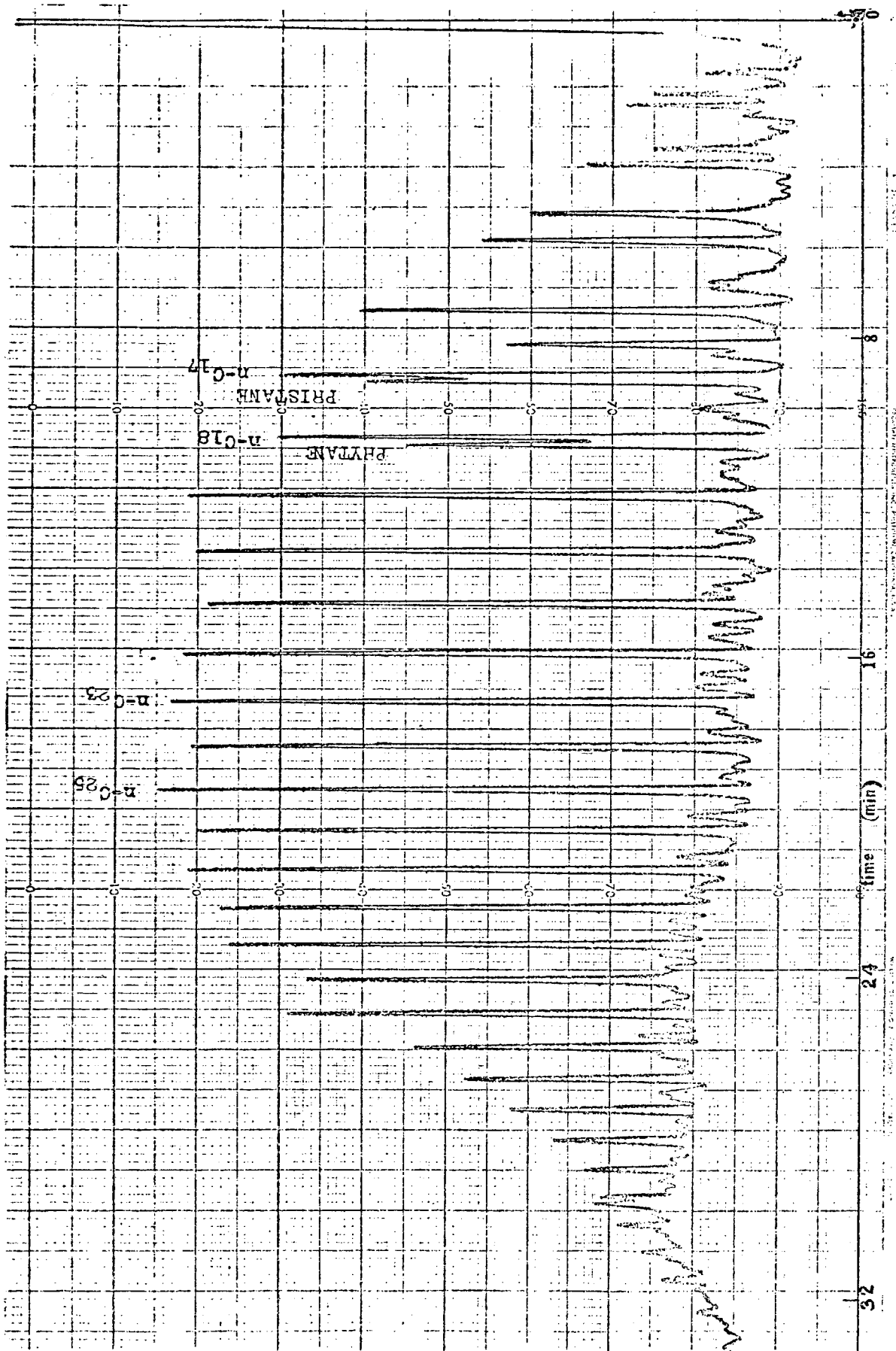


Figure 4. Chromatogram of total saturated fraction of red wash crude oil, lighter fraction.

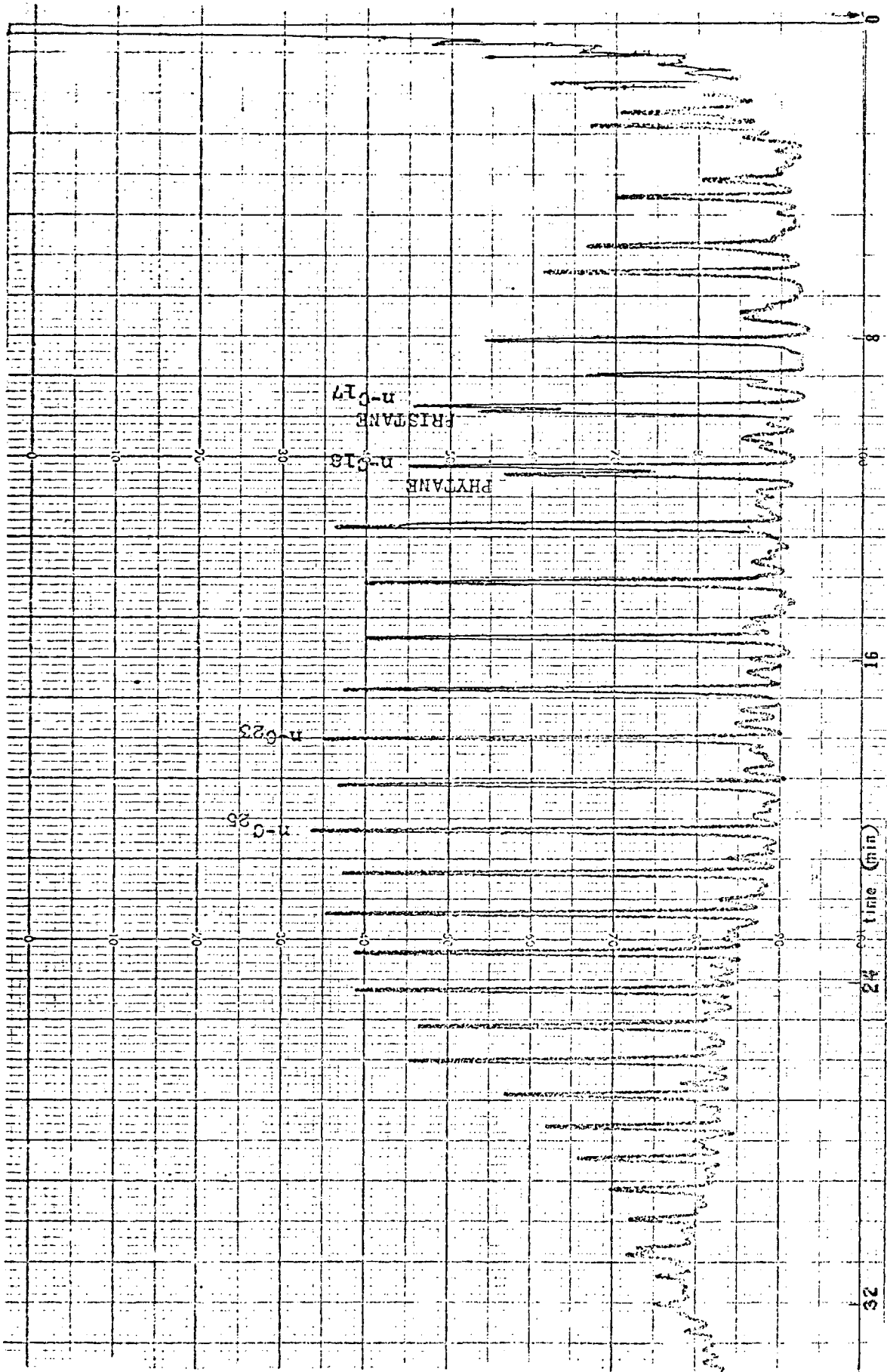


Figure 5. Chromatogram of total saturated fraction of red wash crude oil, heavier fraction.

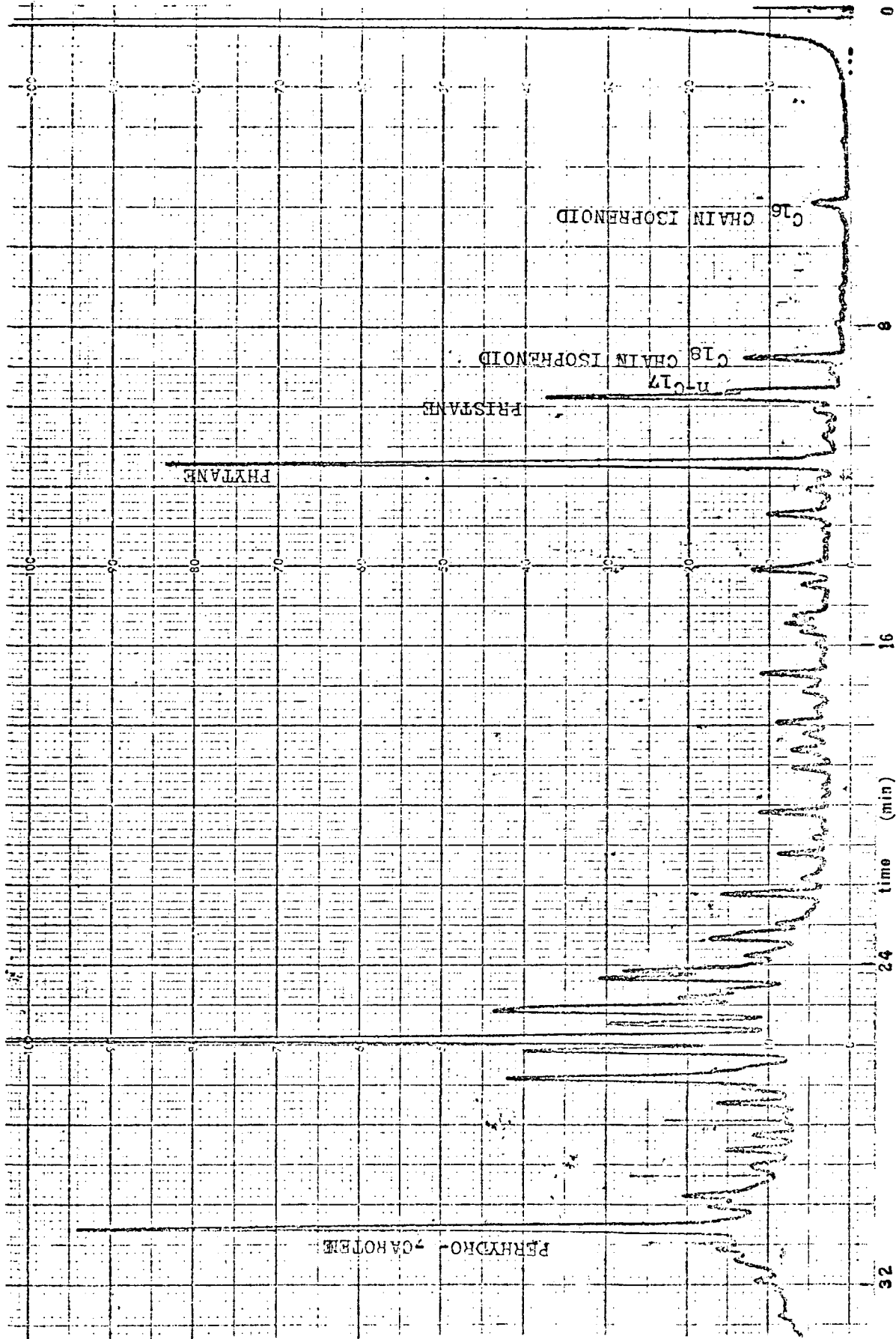


Figure 6. Chromatogram of total saturated fraction of Entire Mahogany Ledge, Parachute Creek, Green River formation.

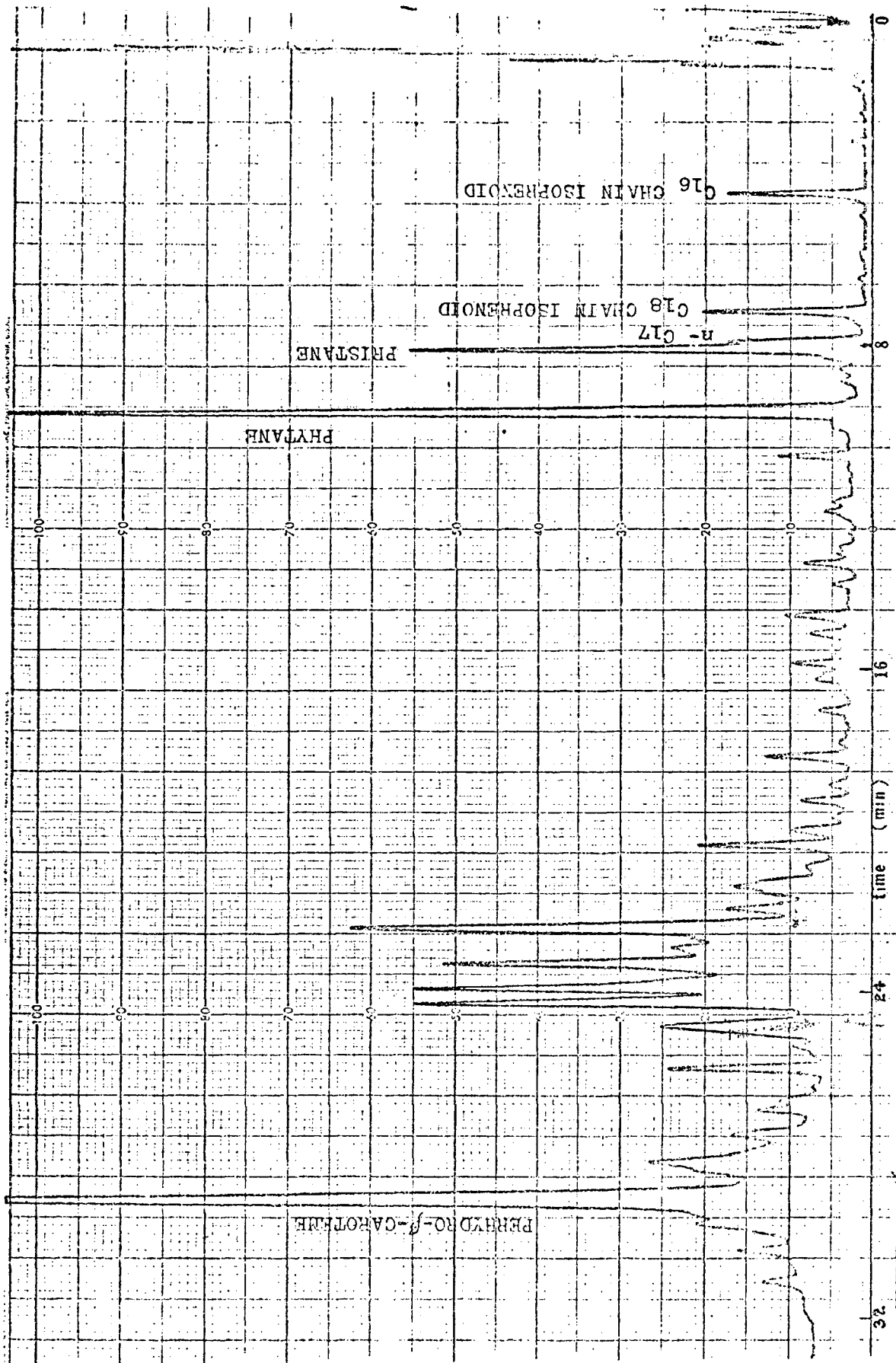


Figure 7. Chromatogram of total saturated fraction of Mahogany Marker, Green River formation.

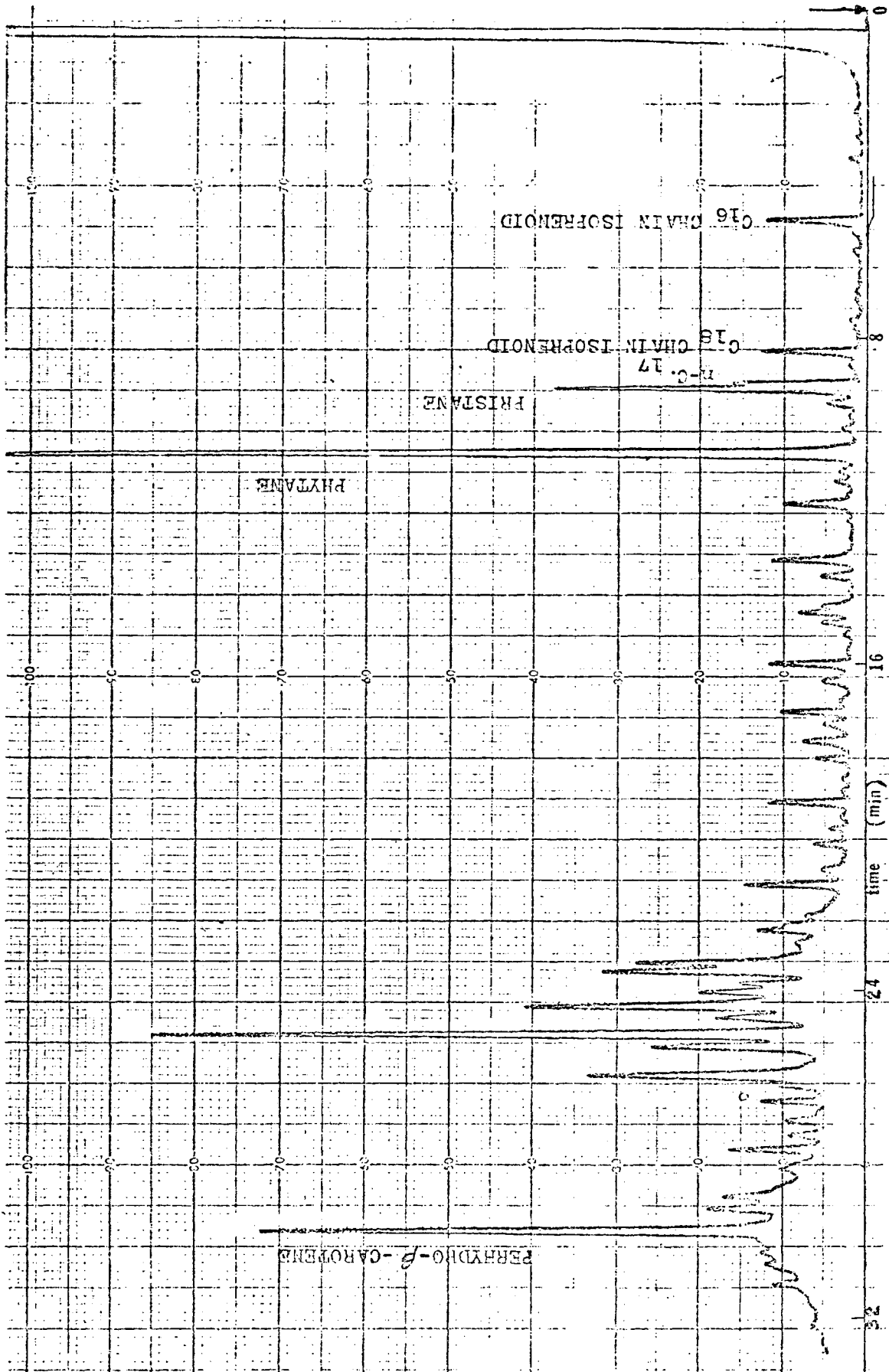


Figure 8. Chromatogram of total saturated fraction of Green River Shale, sample SGK-1 taken by the U. S. G. S.



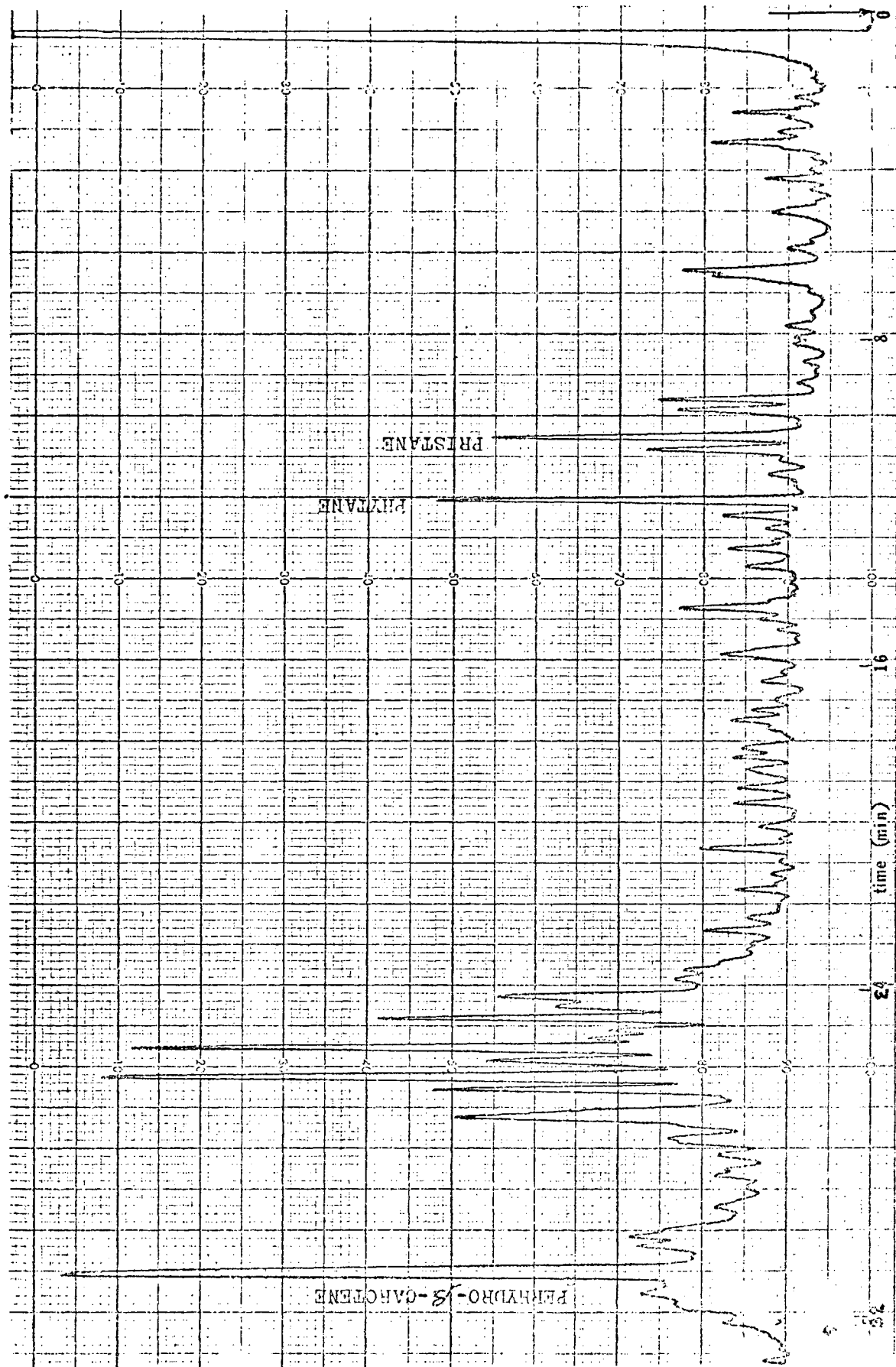


Figure 9. Chromatogram of total saturated fraction of Hillsonite.

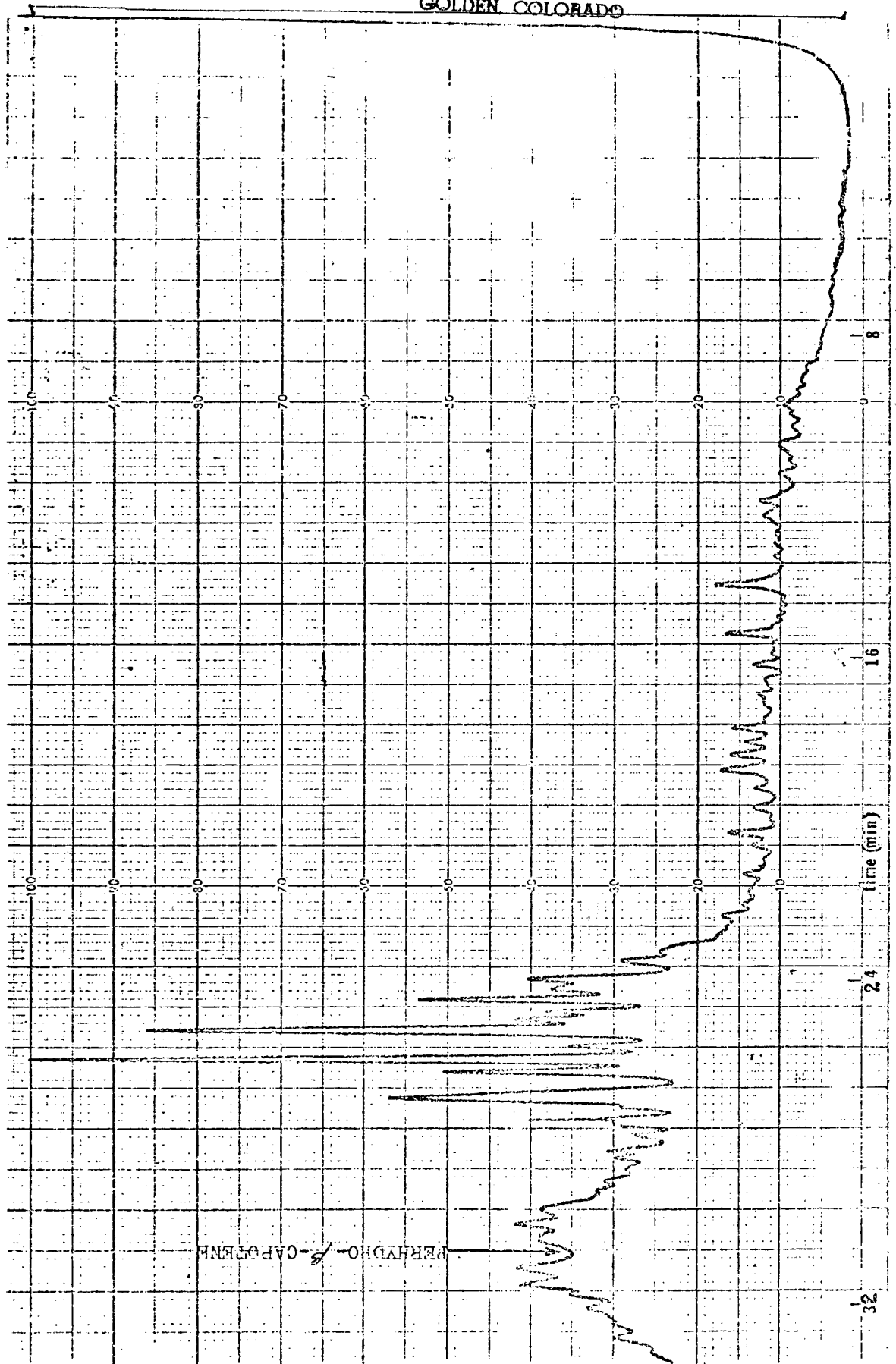


Figure 10. Chromatogram of total saturated fraction of tar sand from Asphalt Ridge, Vernal, Utah.

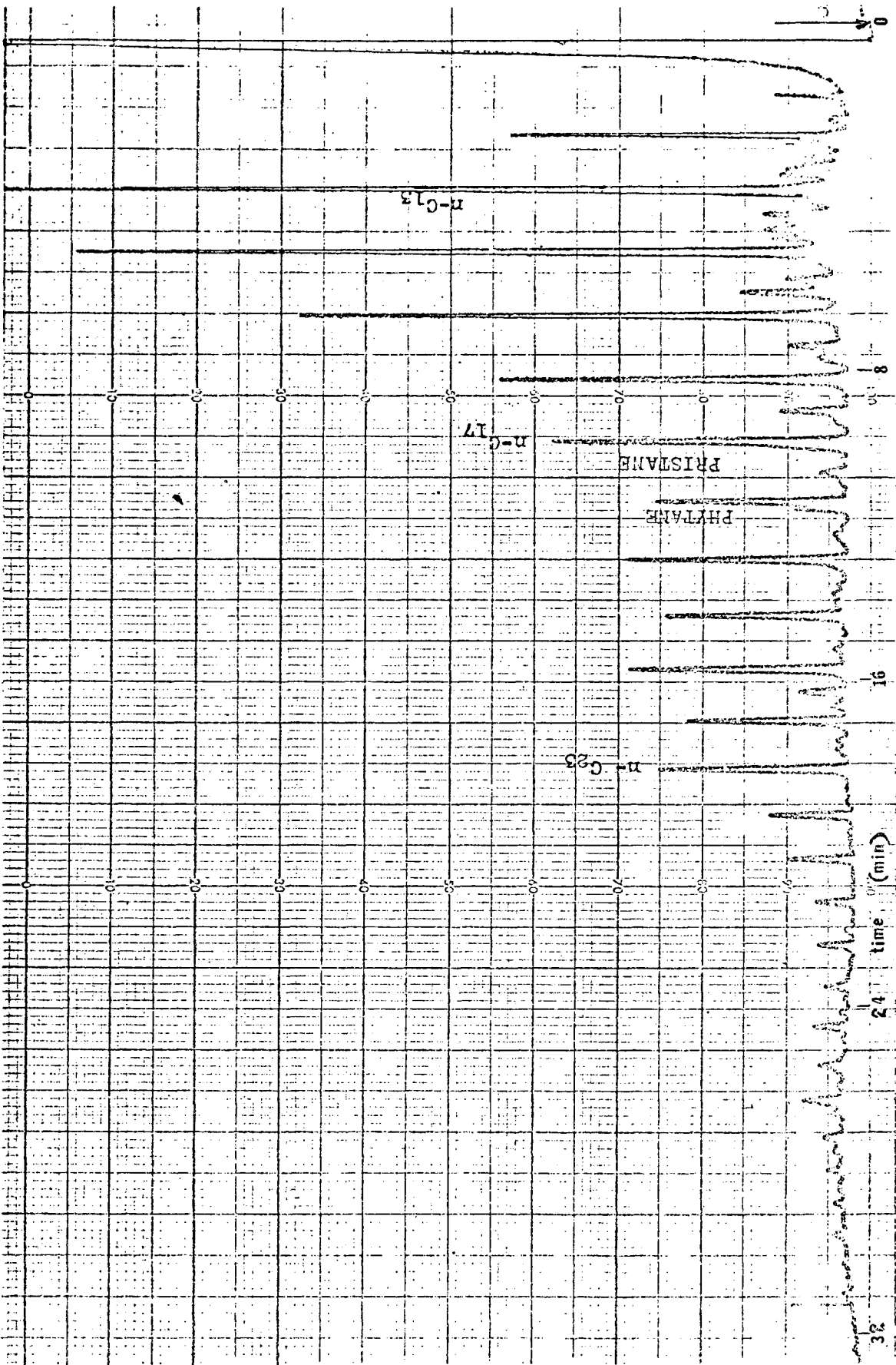


Figure 11. Chromatogram of total saturated fraction of Estonian Shale.

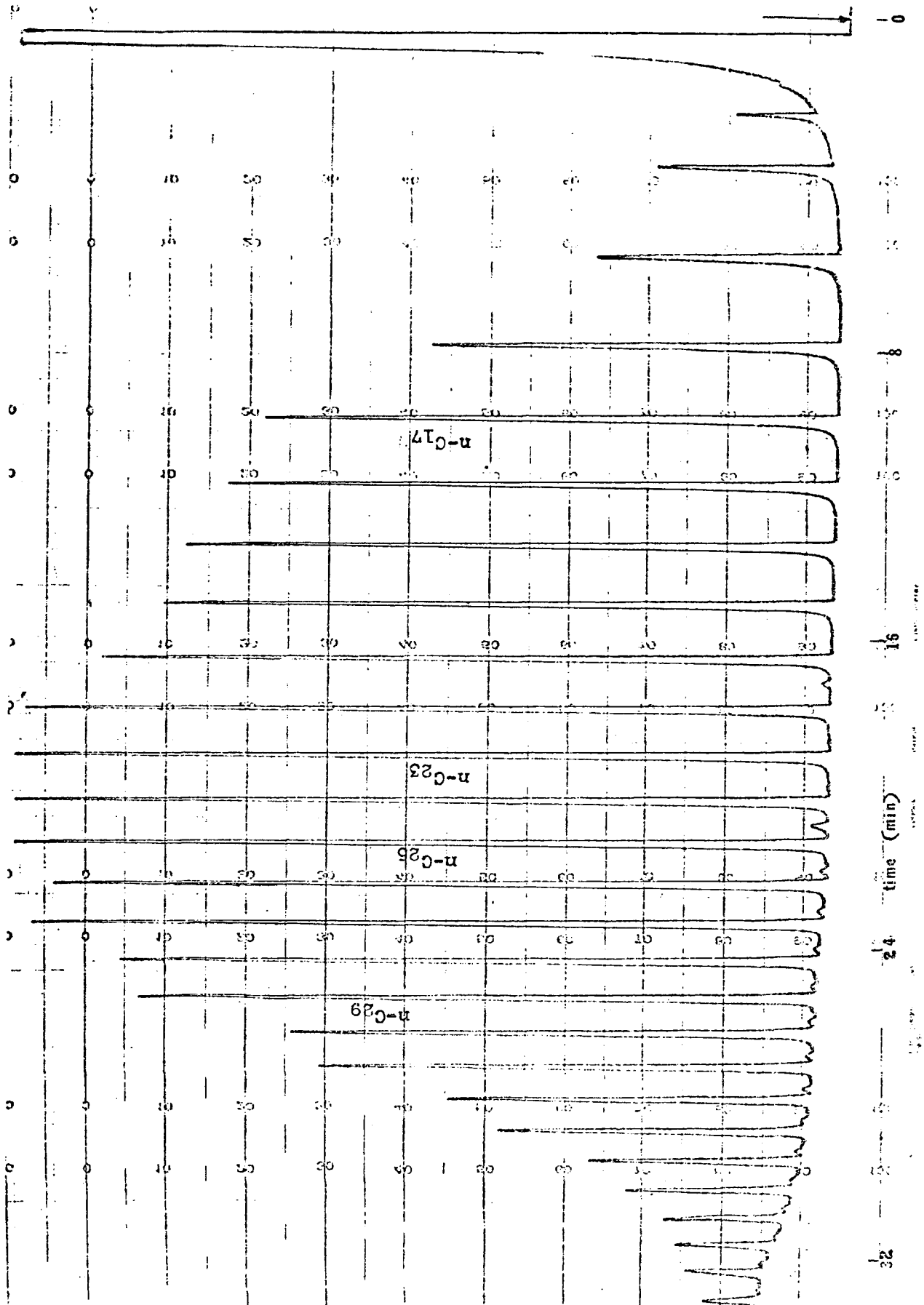


Figure 12. Chromatogram of the normal paraffins fraction of Red Wash crude oil, lighter fraction.

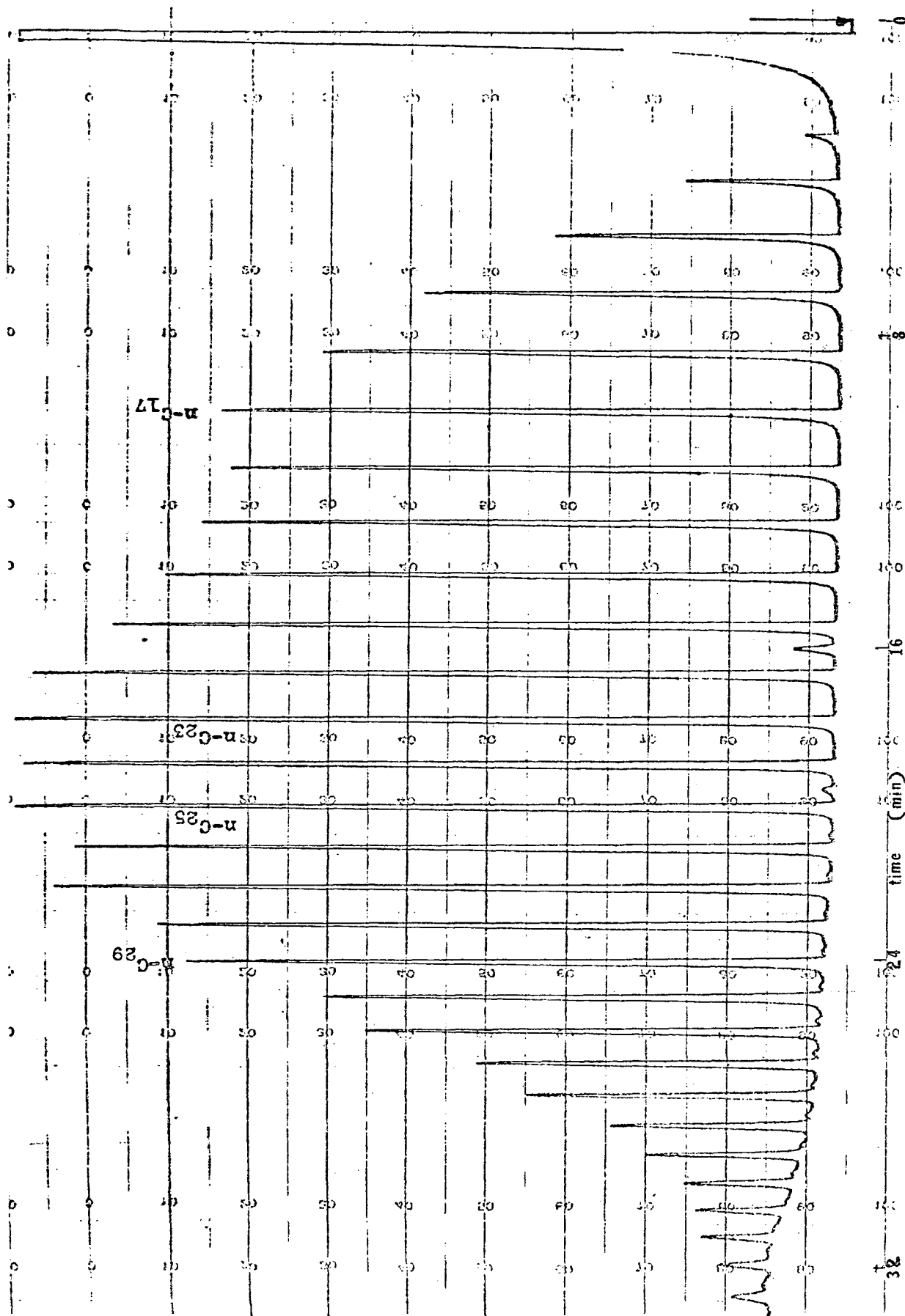


Figure 13. Chromatogram of the normal paraffins fraction of Red Wash crude oil, heavier fraction.

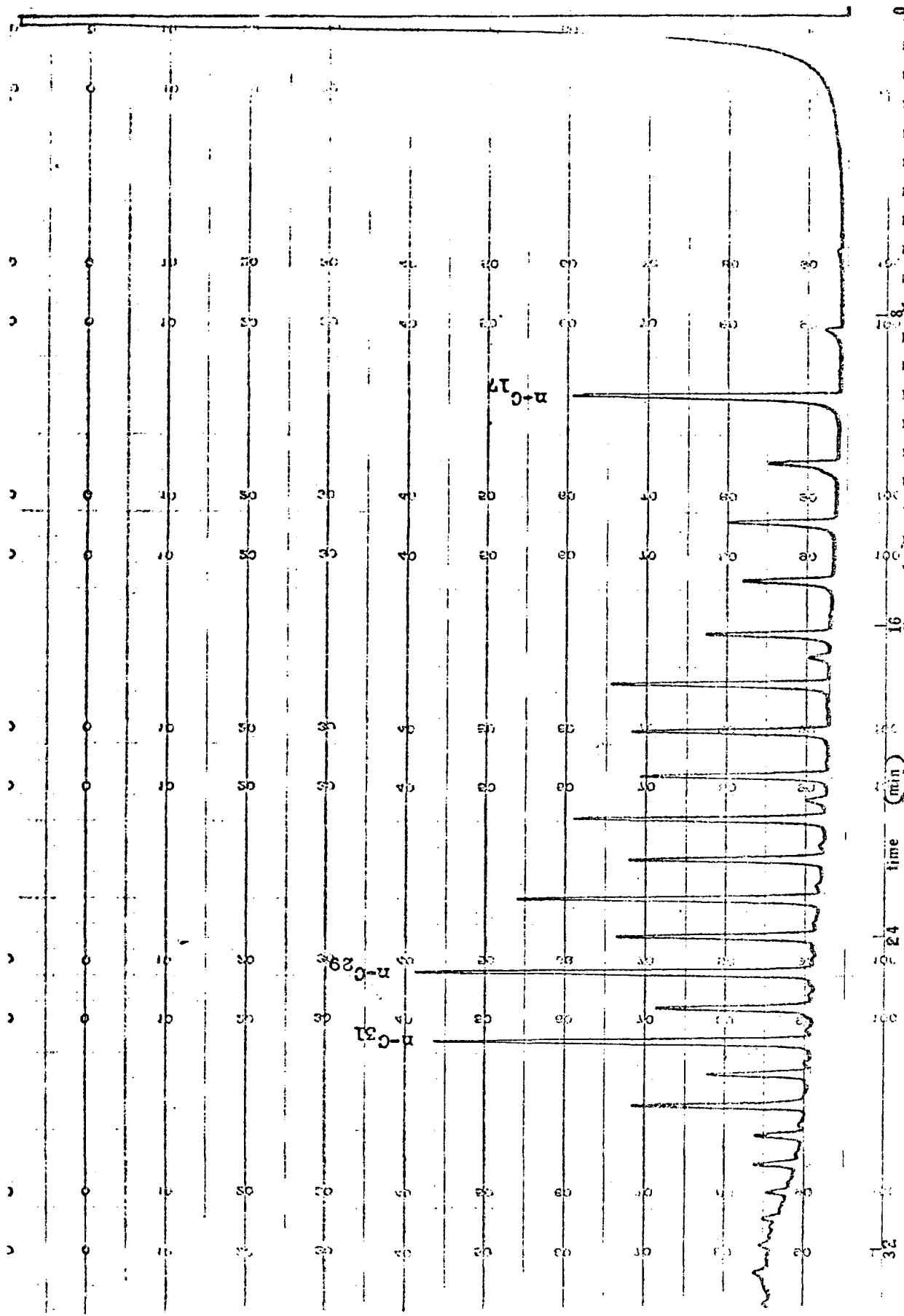


Figure 14. Chromatogram of the normal paraffins fraction of Entire Mahogany Ledge, Parachute Creek, Green River formation.

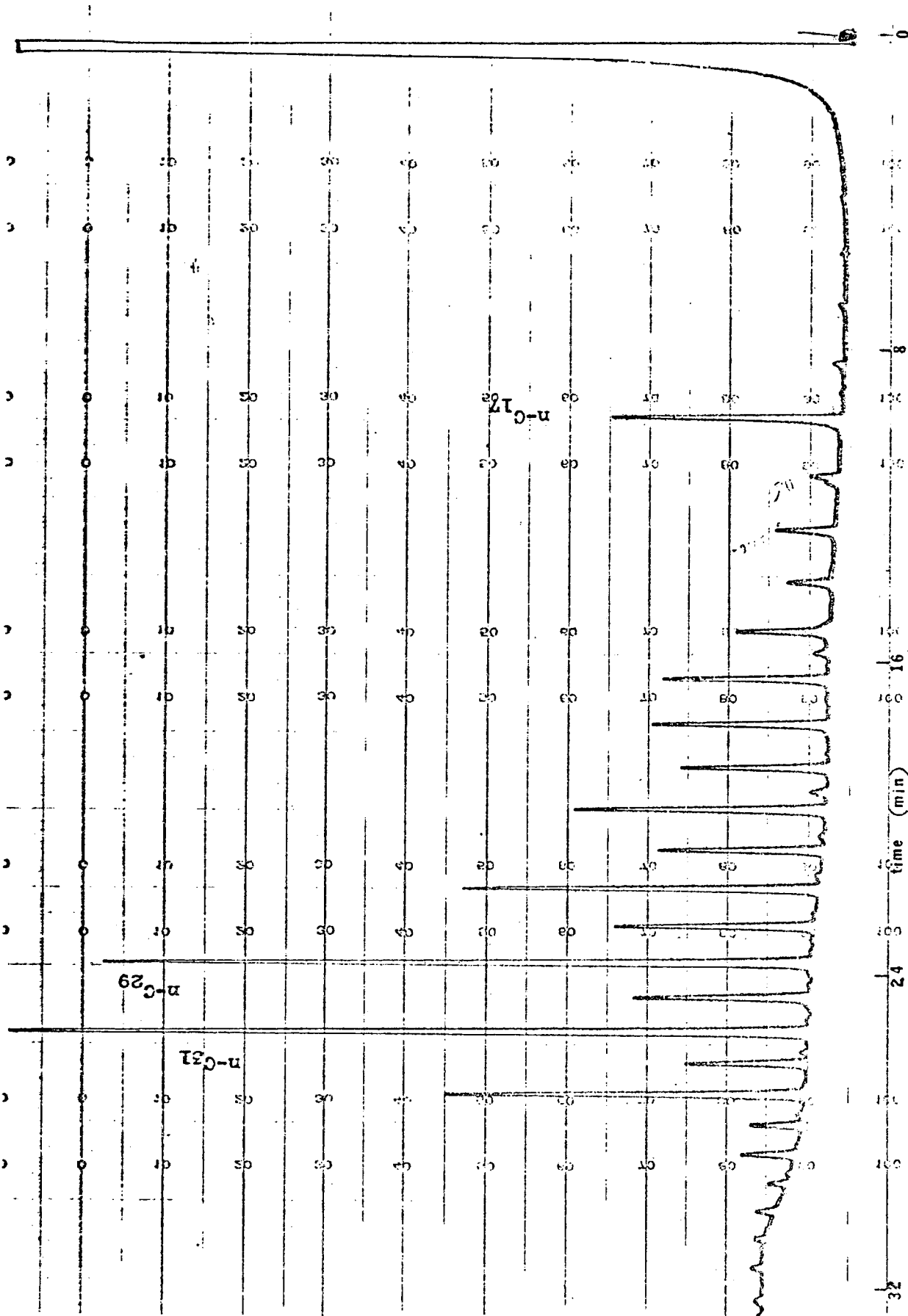


Figure 15. Chromatogram of the normal paraffins fraction of Mahogany Marker, Green River formation.

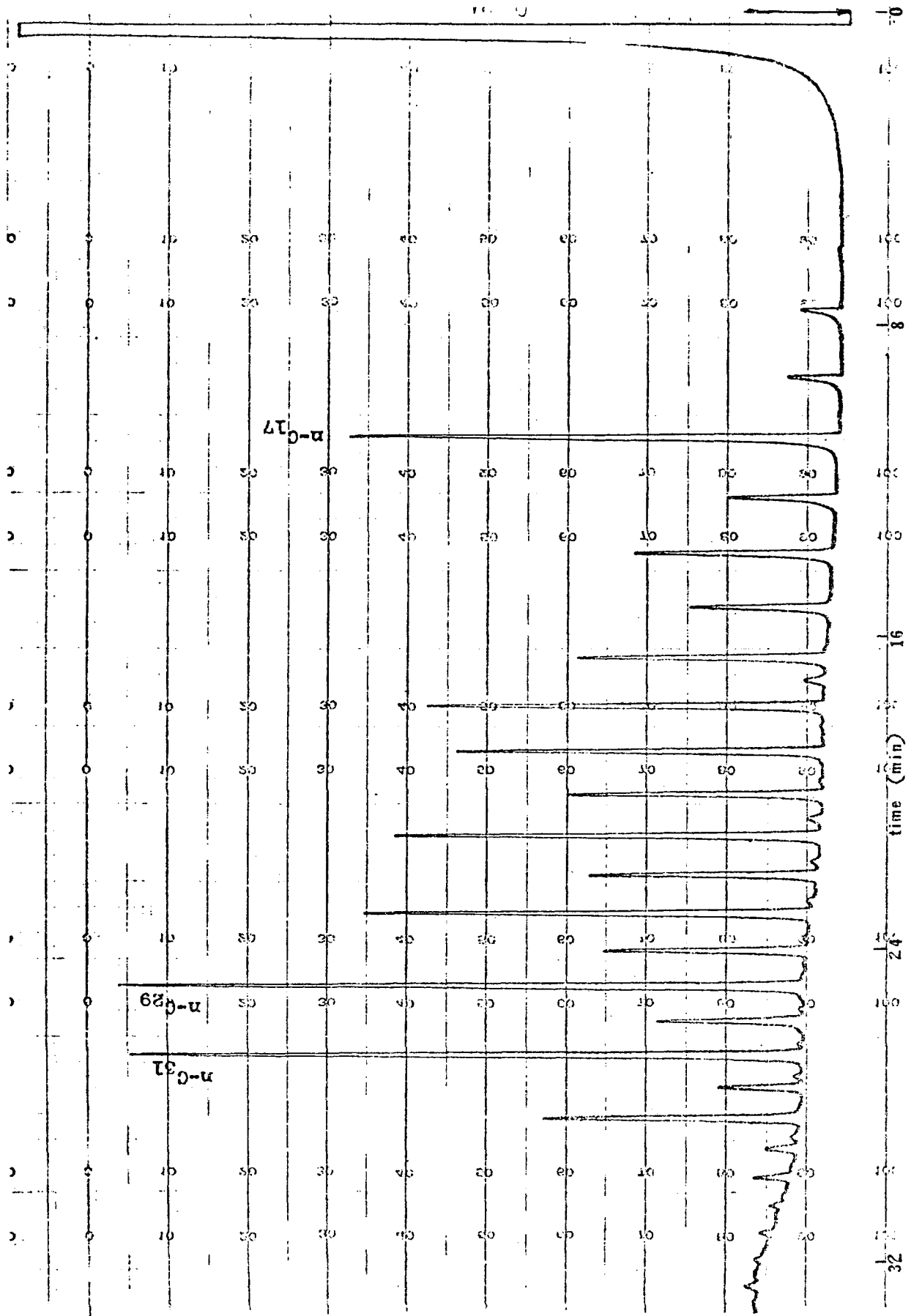


Figure 16. Chromatogram of the normal paraffins fraction of Green River Shale, sample SGR-1 taken by the U. S. G. S.



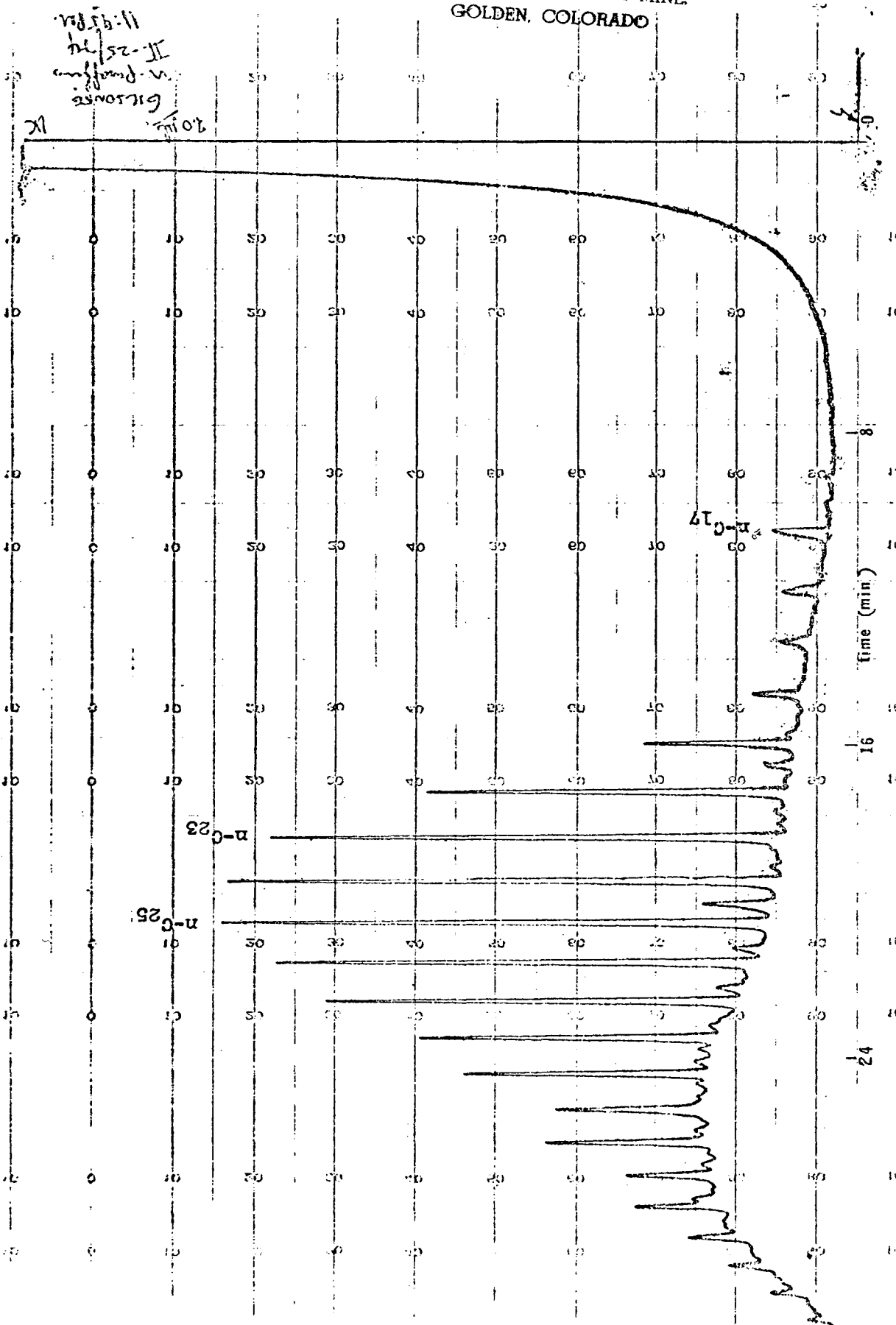


Figure 17. Chromatogram of the normal paraffins fraction of Gilsonite.

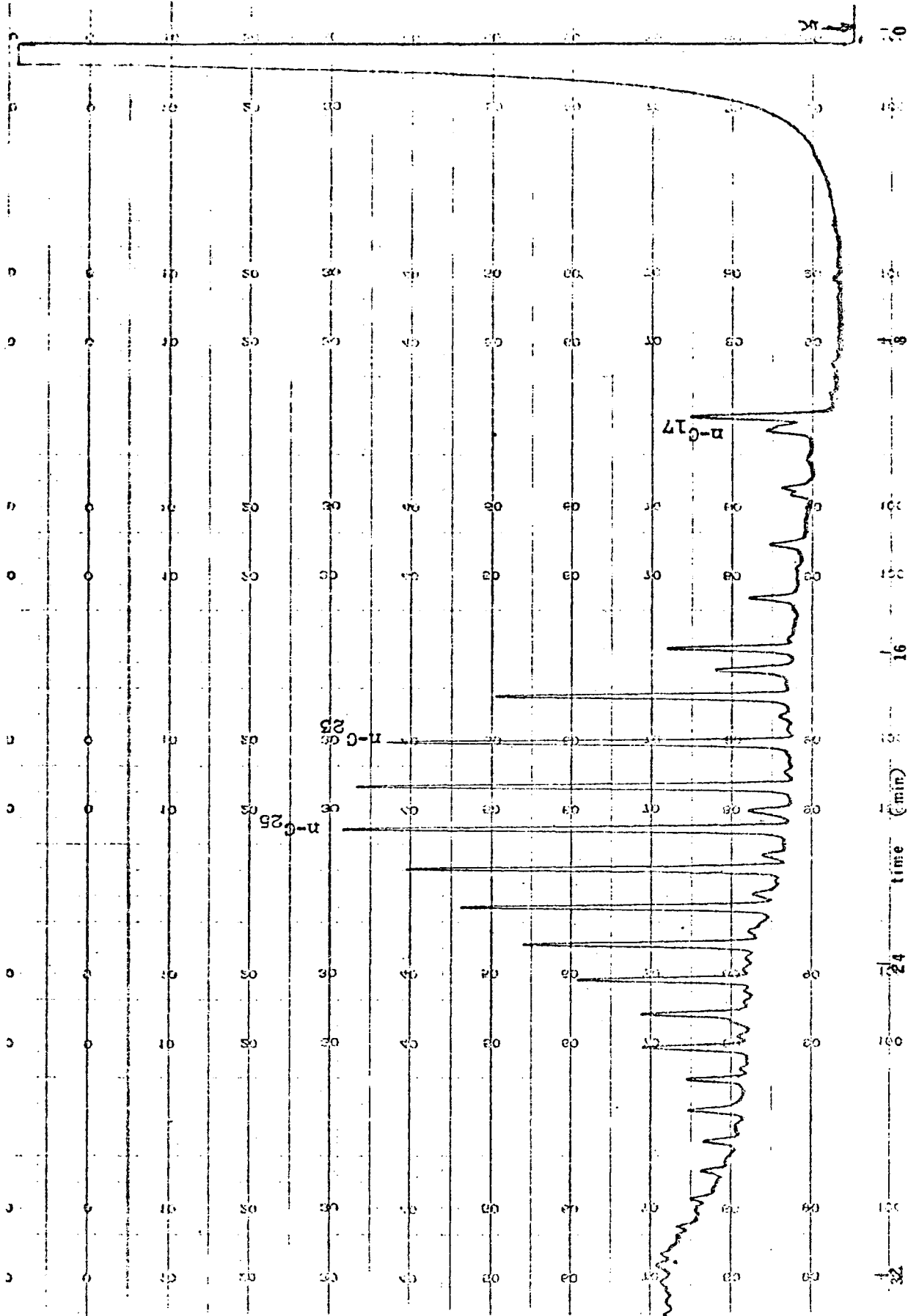


Figure 18. Chromatogram of the normal paraffins fraction of tar sand from Asphalt Ridge, Vernal, Utah.

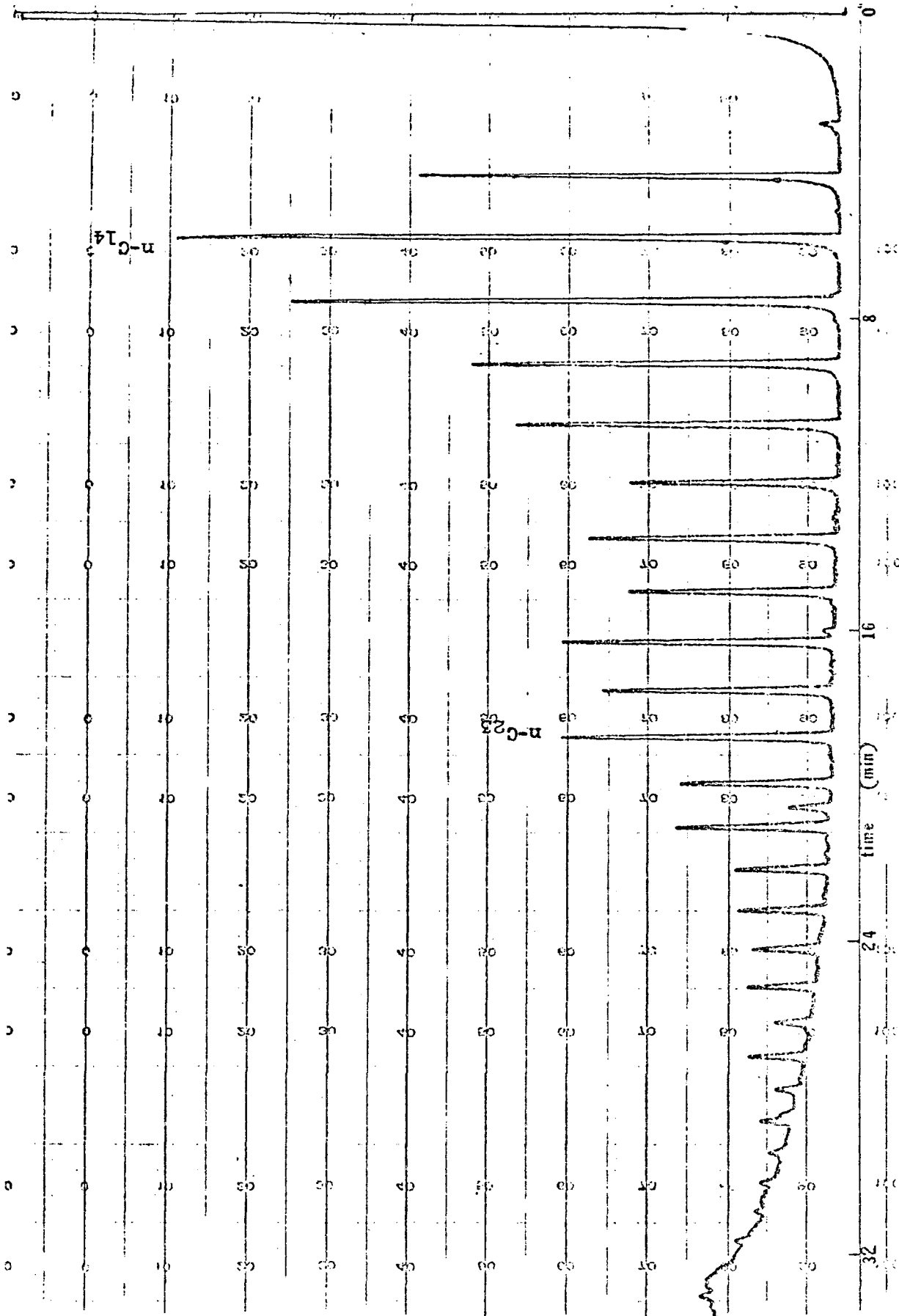


Figure 19. Chromatogram of the normal paraffins fraction of Estonian Shale.

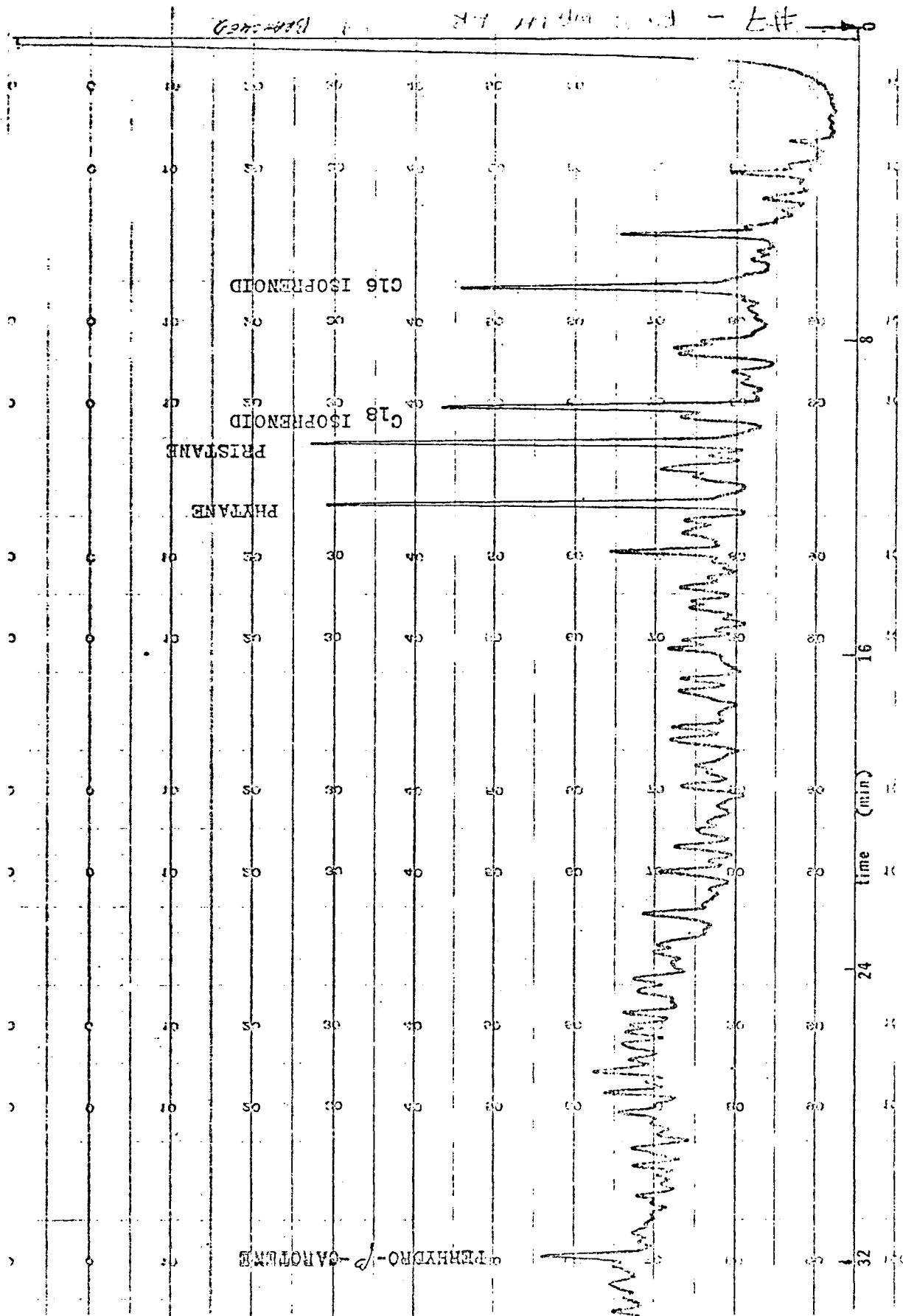


Figure 20. Chromatogram of branched and cyclic fraction of Red Wash crude oil, lighter fraction.

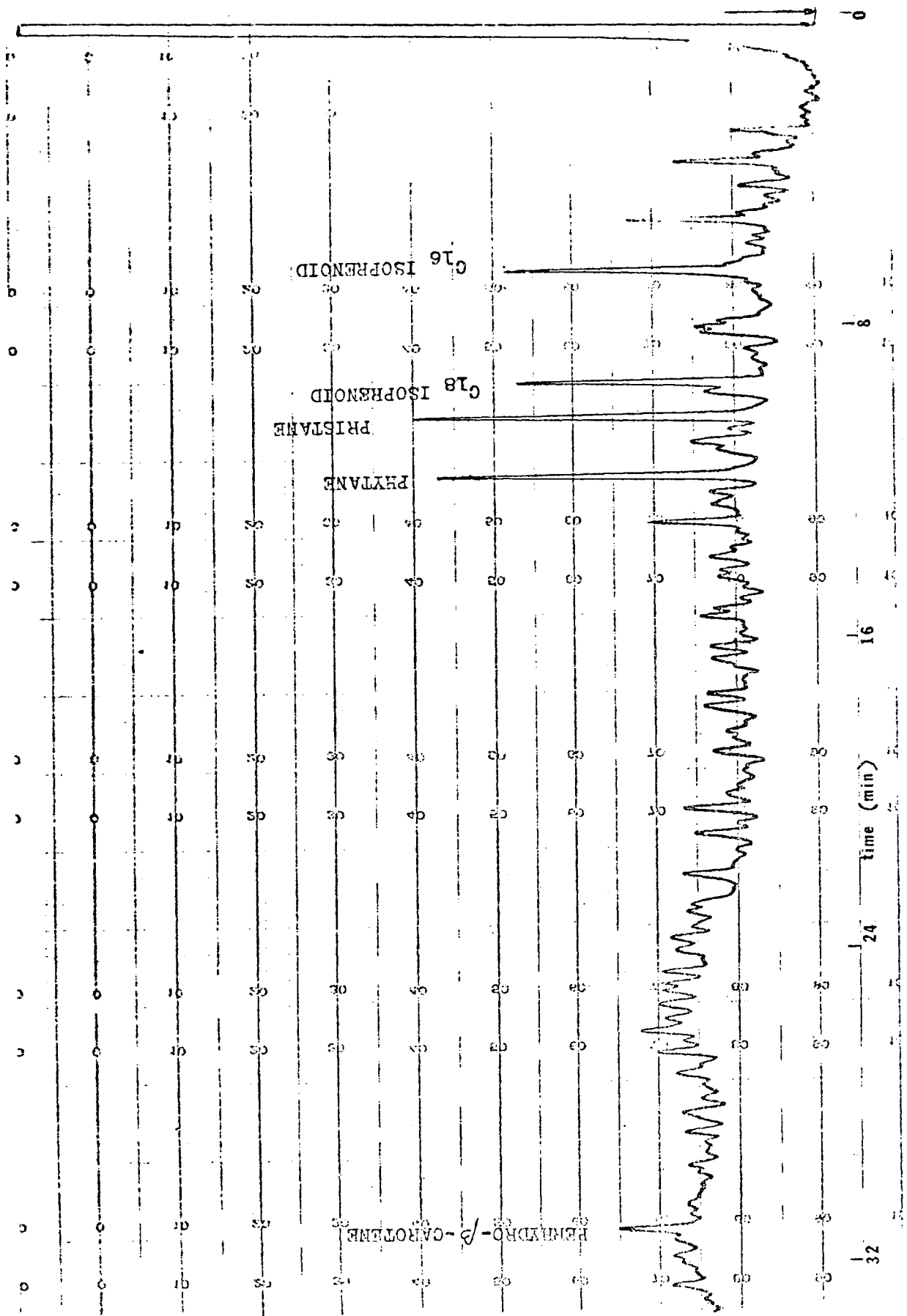


Figure 21. Chromatogram of branched and cyclic fraction of Red Wash crude oil, heavier fraction.

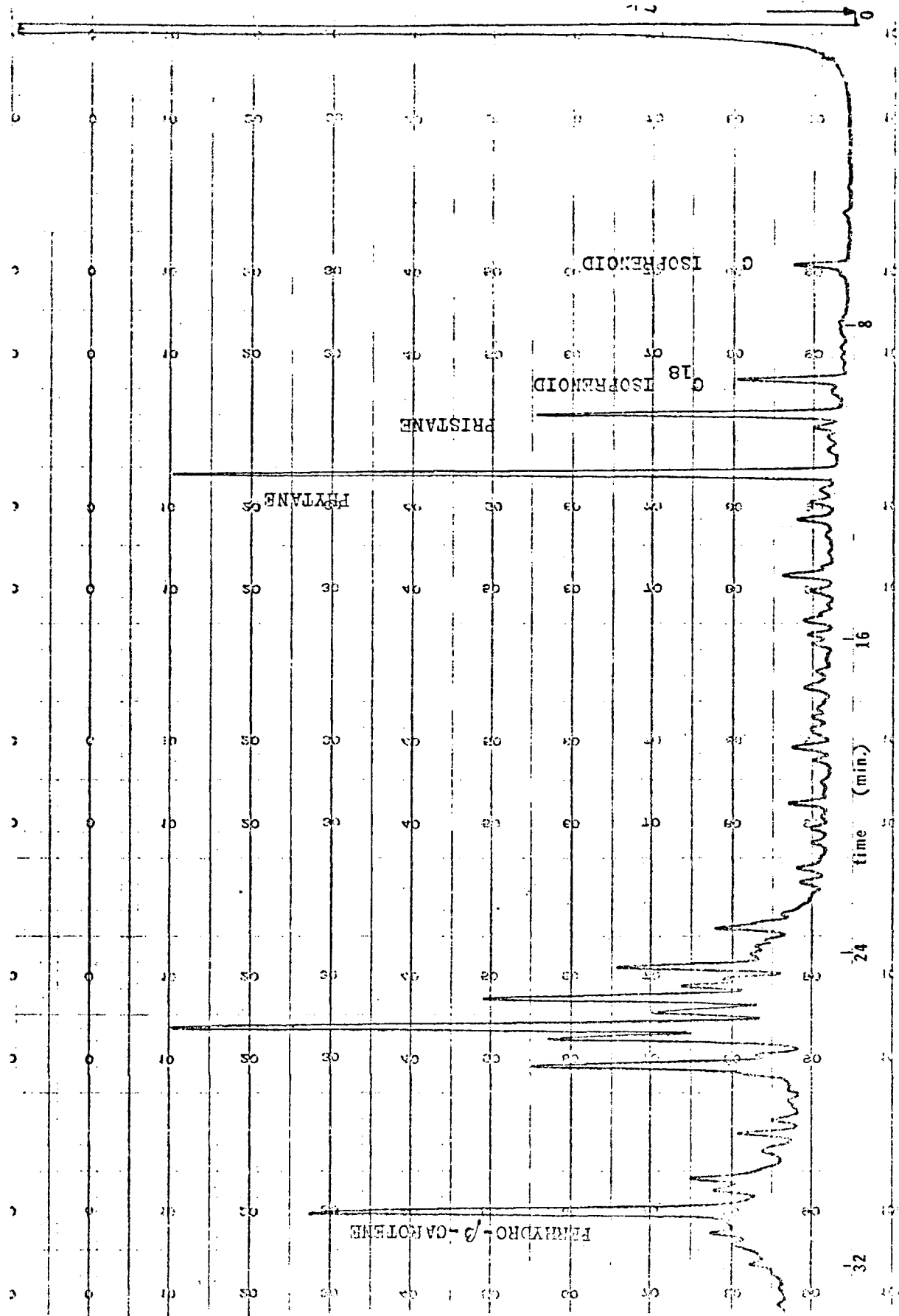


Figure 22. Chromatogram of branched and cyclic fraction of Entire Mahogany Ledge, Parachute Creek, Green River formation.

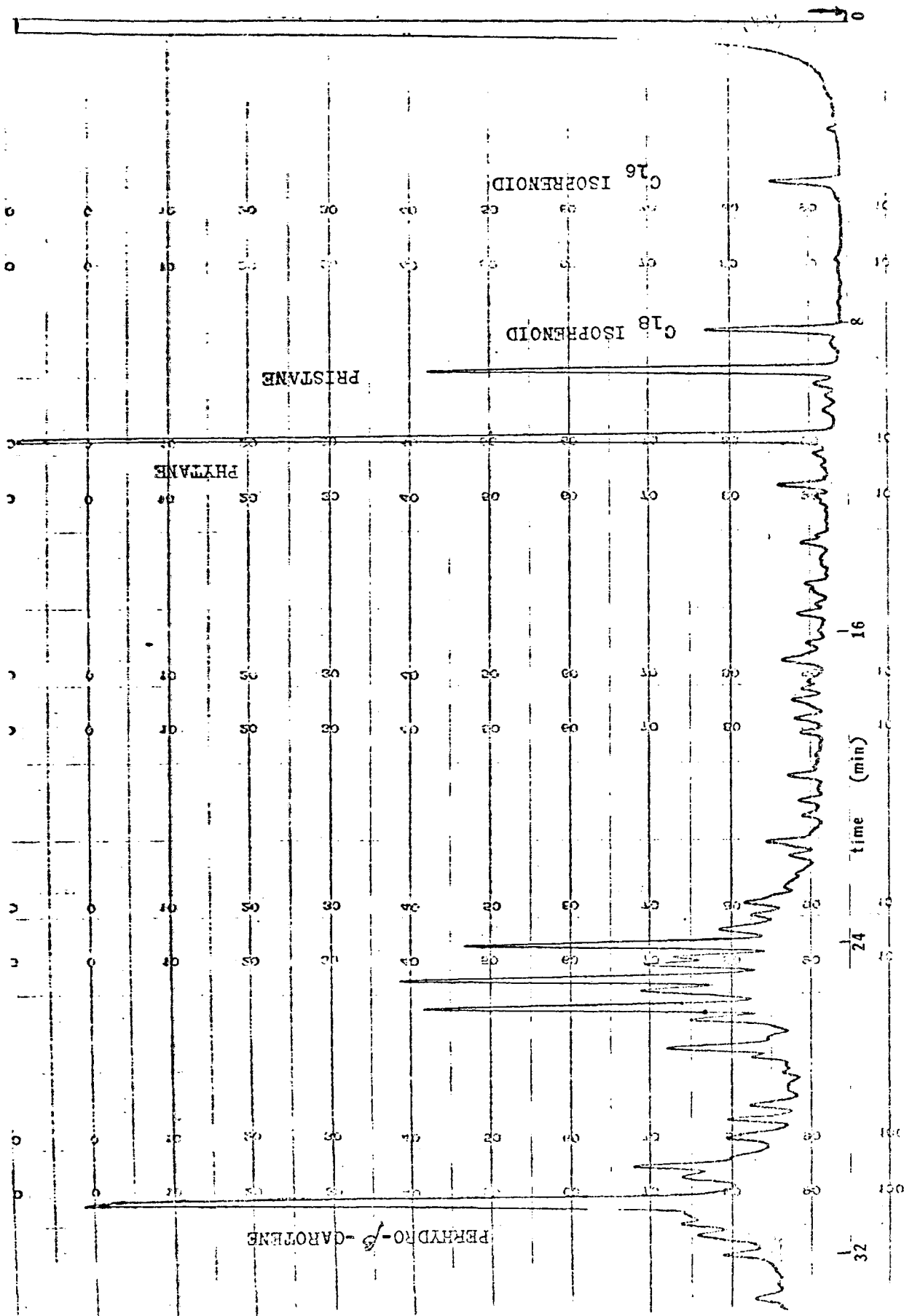


Figure 23. Chromatogram of branched and cyclic fraction of Mahogany Marker, Green River formation.

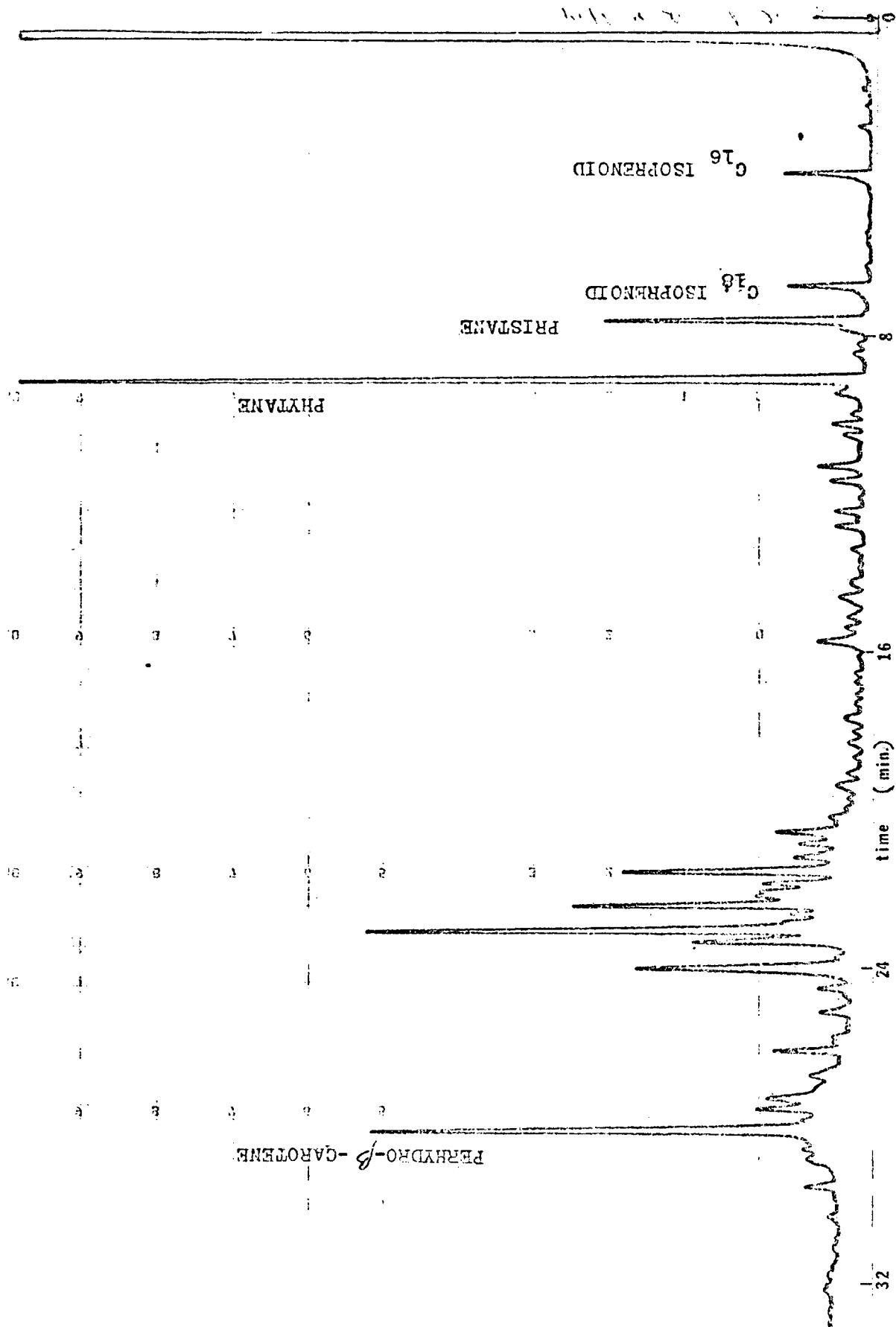


Figure 24. Chromatogram of branched and cyclic fraction of Green River Shale, sample SGR-1 taken by the U. S. G. S.



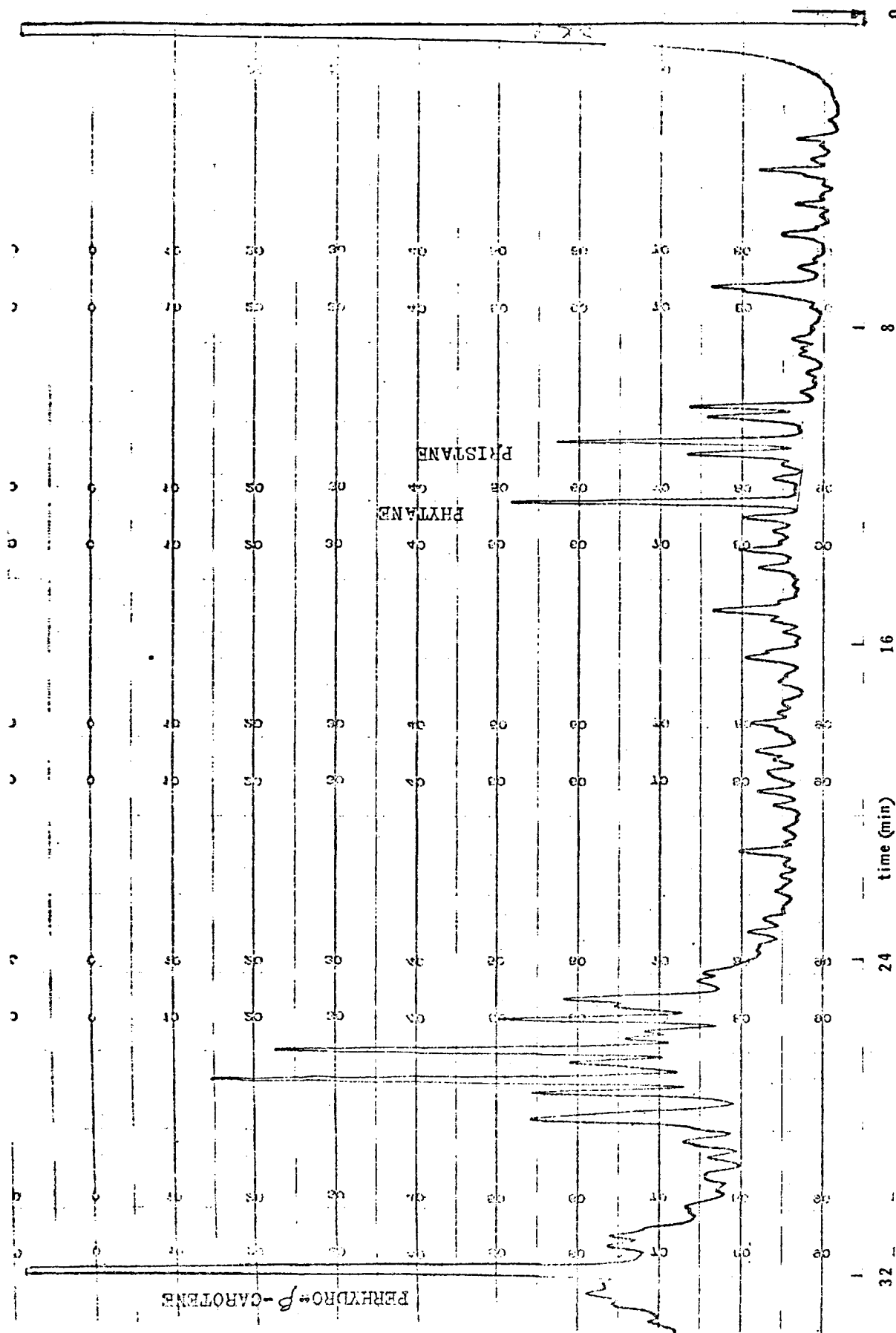


Figure 25. Chromatogram of branched and cyclic fraction of Gilsonite.

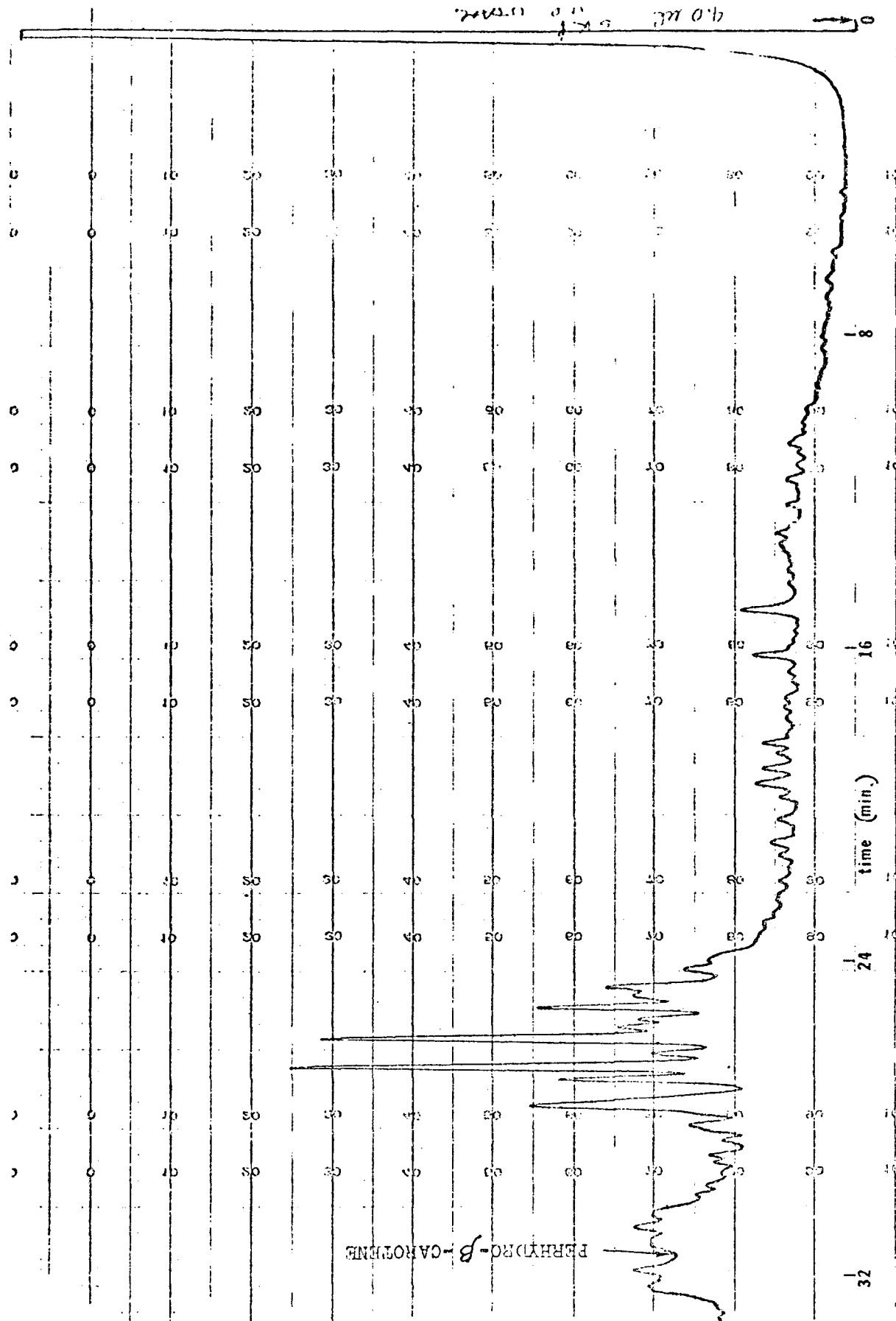


Figure 26. Chromatogram of branched and cyclic fraction of tar sand from Asphalt Ridge, Vernal, Utah.

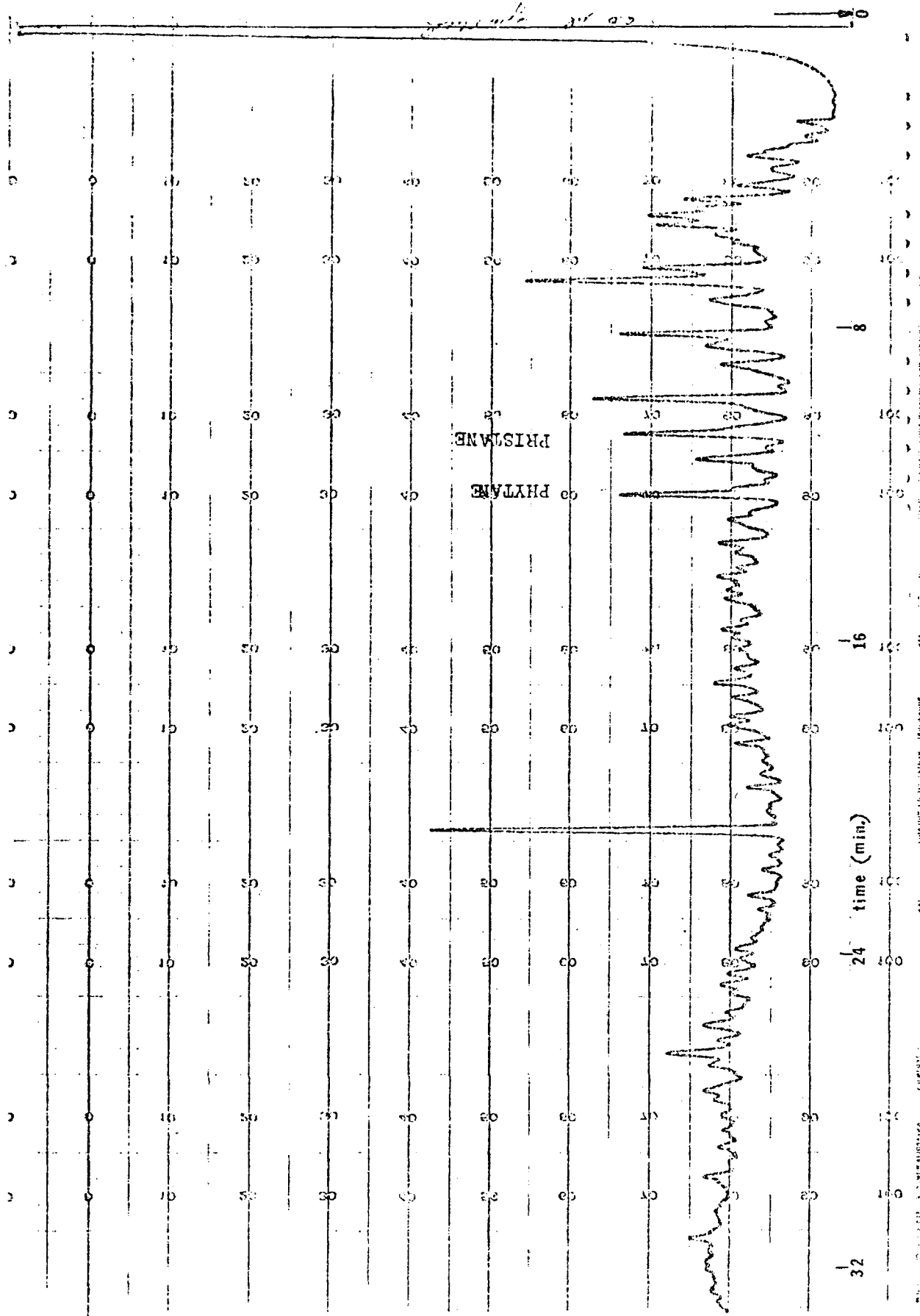


Figure 27. Chromatogram of branched and cyclic fraction of Estonian shale.

BIBLIOGRAPHY

- Akiyama, T., 1972, Chemical composition and molecular weight distribution of dissolved organic matter produced by bacterial degradation of green algae: *Geochem. Jour.*, v. 6, p. 93-104.
- Albretcht, P., and Ourisson, G., 1969, Diagenèse des hydrocarbures saturés dan une Série Sedimentaire Epaisse (Douala, Cameroun): *Geochim. Cosmochim. Acta*, v. 33, p. 138-142.
- Anders, D.E., and Robinson, W.E., 1971, Cycloalkane constituents of the bitumen from Green River shale: *Geochim. Cosmochim. Acta*, v. 35, p. 661-678.
- \_\_\_\_\_, Doolittle, F.G., and Robinson, W.E., 1973a, Analysis of some aromatic hydrocarbons in a benzene soluble bitumen from Green River shale: *Geochim. Cosmochim. Acta*, v. 37, p. 1213-1228.
- \_\_\_\_\_, and Robinson, W.E., 1973b, Geochemical aspects of the constituents of Green River oil shale - Colorado No. 1 core: U.S. Bur. Mines Rept. Inv. RI-7492.
- Anderson, P.C., Gardner, P.M., Whitehead, E.V., Anders, D.E. and Robinson, W.E., 1969, The isolation of steranes from Green River oil shale: *Geochim. Cosmochim. Acta*, v. 33, p. 1304-1307.
- Bailey, N.J.L., Krouse, H.R., Evans, C.R., and Rogers, M.A., 1973, Alteration of crude oils by waters and bacteria: evidence from geochemical and isotope studies: *Am. Assoc. Petroleum Geologists Bull.*, v. 57, no. 7, p. 1276-1290.
- Breger, I.A., 1960, Diagenesis of metabolites and a discussion of the origin of petroleum hydrocarbons: *Geochim. Cosmochim. Acta*, v. 19, p. 297-308.
- Brunnock, J.V., 1966, Separation and distribution of normal paraffins from petroleum heavy distillates by molecular sieve adsorption and gas chromatography: *Anal. Chemistry*, v. 38, no. 12, p. 1648-1652.
- Burlingame, A.L., Haug, P., Belsky, T., and Calvin, M., 1965, Occurrence of biogenic steranes and pentacyclic triterpanes in an Eocene shale (52 million years) and in an early Precambrian shale (2.7 billion years): a preliminary report: *Natl. Acad. Sci. Proc.*, v. 54, p. 1406-1411.

- Calvin, M., 1969, Chemical evolution: Oxford University Press, Oxford.
- Cashion, W.B., and Brown, J.H., Jr., 1956, Geology of the Bonanza-Bragon oil shale area, Uintah County, Utah, and Rio Blanco County, Colorado: U.S. Geol. Survey Oil and Gas Inv. Map OM-153.
- Cashion, W.B., 1967, Geology and fuel resources of the Green River formation, southeastern Uinta Basin, Utah and Colorado: U.S. Geol. Survey Prof. Paper 548.
- Cooper, J.E., 1962, Fatty acids in recent and ancient sediments and petroleum reservoir waters: *Nature*, v. 193, p. 744-746.
- \_\_\_\_\_, and Bray, E.E., 1963, A postulated role of fatty acids in petroleum formation: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 8, no. 2, p. A17-A27.
- Covington, R.E., 1957, The bituminous sandstones of the Asphalt Ridge area, northeastern Utah: Intermountain Assoc. of Petroleum Geologists, 8th Ann. Field Conf., p. 172-175.
- \_\_\_\_\_, 1964, Bituminous sandstone and limestone deposits of Utah: *Utah Geol. and Mineralog. Survey Bull.*, p. 221-248.
- Crawford, A.L., and Pruitt, R.G., 1963, Gilsonite and other bituminous resources of Central Uintah County, Utah, in
- Cummings, J.J., and Robinson, W.E., 1963, Normal and iso-prenoid hydrocarbons isolated from oil-shale bitumen: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 8, no. 3, p. 97-103.
- Davis, L.J., 1968, Geology of Gilsonite: Intermountain Assoc. of Petroleum Geologists, 8th Ann. Field Conf., p. 152-156.
- Davis, J.W., and Johnson, R.T., 1968, Petroleum hydrocarbons formed by irradiation of a simulated sediment: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 13, no. 4, p. B26-B31.
- Didyer, B.M., Ober, G., and McCarthy, E.D., 1972, "Fingerprinting" the migration of a Chilean oil: *Geochim. Cosmochim. Acta*, v. 37, p. 1402-1406.

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- Donnell, J.R., Culbertson, W.C., and Cashion, W.B., 1967, Oil shale in the Green River formation, in Occurrence and Prospects of Oil Shale, P.D. 14(7), 7<sup>o</sup> Congreso Mundial del Petroleo, Mexico.
- Duncan, D.C., 1967, Geologic setting of oil shale deposits and world prospects, in Occurrence and Prospects of Oil Shales, P.D. 14(1), 7<sup>o</sup> Congreso Mundial del Petroleo, Mexico.
- Eglinton, G., Scott, P.M., Belsky, T., Burlingame, A.L., and Calvin, M., 1964, Hydrocarbons of biological origin from a one-billion-year-old sediment: Science, v. 145, p. 263-264.
- \_\_\_\_\_, Douglas, A.G., Maxwell, J.R., Ramson, J.N., and Stallberg-Stehagen, S., 1966, Occurrence of isoprenoid fatty acids in the Green River shale: Science, v. 153, p. 1133-1134.
- Fabre, M., Guichard-Loudet, N.J., and Roucache, J.R., 1968, Etude de la repartition dan un petrole brute des n-paraffines c par c de C1 a C40 a l'aide des tamis moleculaires 5A<sup>o</sup> et de la C.P.G., in Schenck, P.A., and Havenaar, I., eds., 1968, Advances in Organic Geochemistry: London, Pergamon Press, v. 31, p. 241-260.
- Fergusson, W.S., 1962, Analytical problems in determination of hydrocarbons in sediments: Amer. Assoc. Petroleum Geologists Bull., v. 46, no. 9, p. 1613-1620.
- Gallegos, E.J., 1970, Identification of new steranes, terpanes and branched paraffins in Green River shale by combined gas chromatography and mass spectrometry: Preprints Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 15, no. 3, p. A39
- Guerrild, P.M., 1972, Genesis of oil in metalliferous veins, San Juan Mountains, Colorado: M. Sc. Thesis, Colorado School of Mines, T-1434, 60 pp.
- Han, J., McCarthy, E.D., Hoeven, W.V., Calvin, M., and Bradley, W.H., 1968, Organic geochemical studies II. A preliminary report on the distribution of aliphatic hydrocarbons in algae, in bacteria, and in a recent lake sediment., Natl. Acad. Sci. Proc., v. 59, p. 29-33.

- Hedberg, H.D., 1964, Geologic aspects of origin of petroleum: Amer. Assoc. Petroleum Geologists, v. 48, no. 11, p. 1755-1803.
- Henderson, J.H., Jr., 1957, The Gilsonite refining project of the American Gilsonite Co., : in Guidebook to the Geology of the Uinta Basin, Intermountain Assoc. Petroleum Geologists, 8th Ann. Field Conf., p. 157-160.
- \_\_\_\_\_, Eglinton, G., Simmonds, P., and Lovelock, J.E., 1968a, Thermal alteration as a contributory process to the genesis of petroleum: Nature, v. 219, p. 1013-1016.
- \_\_\_\_\_, and Steel, 1971, Isolation and characterization of a tripernoid alcohol from the Green River shale, Chem. Comm., p. 1331-1332.
- Hills, I.R., Smith, G.W., and Whitehead, E.V., 1968, Hydrocarbons from fossil fuels and their relationship with living organisms: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 13, no. 4, p. B4-B18.
- Hodgson, G.W., and Ponnampetuma, C., 1968, Prebiotic porphyrin genesis: porphyrins from electric discharge in methane, ammonia and water vapor: Natl. Acad. Sci. Proc., v. 59, p. 22-
- Hunt, J.M., Stewart, F., and Dickey, P.A., 1954, Origin of hydrocarbons of Uinta Basin, Utah: Amer. Assoc. Petroleum Geologist, v. 38, no. 8, p. 1671-1698.
- \_\_\_\_\_, 1963, Composition and origin of the Uinta Basin bitumens: Utah Geol. and Mineralog. Survey Bull., v. 54, p. 249-273.
- Johnson, R.W., 1973, Early diagenesis of fatty acids in a salt marsh environment: Geochim. Cosmochim. Acta, v. 37, p. 1943-1955.
- Jurg, J.W., and Eisma, E., 1964, Petroleum hydrocarbons: generation from fatty acids, Science, v. 144, p. 1451.
- Kayser, R.B., 1966, Bituminous sandstones deposits, Asphalt Ridge: Utah Geol. and Mineralog. Survey, Special Studies no. 19, 62 pp.
- Kogerman, P.N., Kopwillmem, J., 1932, Hydrogenation of Esthonian oil shale and shale oil: Jour. of the Institution of Petroleum Technologists, v. 18, p. 833-845.

- Koons, Ch. B., Kamieson, G.W., and Cierezko, L.S., 1965, Normal alkane distributions in marine organisms: possible significance to petroleum origin: Amer. Assoc. Petroleum Geologists Bull., v. 49, p. 301-316.
- Krogmann, D.N., 1973, The biochemistry of green plants: Prentice Hall Inc., Englewood Cliffs, New Jersey.
- Kvenvolden, K.A., 1966, Molecular distribution of normal fatty acids and paraffins in some lower Cretaceous sediments, Nature, v. 209, p. 573-577.
- Lawlor, D.L., Robinson, W.E., 1965, Fatty acids in Green River formation oil shale, Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 10, no. 1, p. 5-7.
- Martin, R.L., Winters, J.C., and Williams, J.A., 1963, Distribution of normal paraffins in crude oils and their importance to origin of petroleum: Nature, v. 199, p. 110-113.
- McNair, H.M., and Bonelli, E.J., 1969, Basic gas chromatography: Varian Aerograph, eds., Palo Alto, California.
- Meinschein, W.G., 1959, Origin of petroleum: Amer. Assoc. Petroleum Geologists, v. 43, no. 5, p. 925-943.
- Murphy, M.T.J., McCormick, A., Eglinton, G., 1967, Perhydro  $\beta$ -carotene in the Green River shale: Science, v. 157, p. 1040-1042.
- O'Connor, J.G., Burrow, F.H., and Norris, M.J., 1962, Determination of normal paraffins in C-20 to C-32 paraffins waxes by molecular sieve adsorption: Anal. Chemistry, v. 34, no. 1, p. 82-85.
- Picard, M.D., 1957, The Red Wash-Walker Hollow field - A resume: in A Guidebook to the Geology of the Uinta Basin, Intermountain Assoc. of Petroleum Geologists, 8th Ann. Field Conf. (1957).
- Philippi, G.T., 1965, On the depth, time and mechanism of petroleum generation: Geochim. Cosmochim. Acta, v. 29, p. 1021-1049.
- \_\_\_\_\_, 1968, Essentials of the petroleum formation process are organic source material and a subsurface temperature controlled chemical reaction mechanism, in Schenk, P.A., and Havenaar, I., Advances in Organic Geochemistry: London, Pergamon Press, v. 31, p. 25-26.



- Ponnamperuma, C., 1968, Abiogenic hydrocarbons: Preprints v. 13, no. 4, p. B21-B22.
- Pruitt, R.B., 1961a, The mineral resources of Uintah County, Utah: Utah Geol. and Mineralog. Survey Bull., v. 71, p. 11.
- Pruitt, R.B., 1961b, Gilsonite in The mineral resources of Uintah County, Utah: Utah Geol. and Mineralog. Survey Bull., v. 71, p. 23-49.
- Robinson, W.E., Cummings, J.J., and Dinneen, G.U., 1965, Changes in Green River oil-shale paraffins with depth: Geochim. Cosmochim. Acta, v. 29, p. 249-258.
- \_\_\_\_\_, 1969, Kerogen of the Green River formation, in Eglinton, G., and Murphy, M.T.J., eds., Organic Geochemistry methods and results: Springer-Verlag, New York - Heidelberg - Berlin.
- \_\_\_\_\_, and Cook, 1971, Compositional variations of the organic material of Green River oil shale - Colorado No. 1 core: U.S. Bur. Mines Rept. Inv. R1-7492.
- Rudakov, G., 1967, Recent developments in the theory of the non-biogenic origin of petroleum: Chem. Geol., v. 2, p. 179-185.
- Scalan, R.S., and Smith, J.E., 1970, An improved measure of the odd-even predominance in the normal alkanes of sediment and petroleum: Geochim. Cosmochim. Acta, v. 34, p. 611-620.
- Schrayer, G.J., 1968, Current views on the origin of petroleum: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., v. 13, no. 4, p. B40-B42.
- Shimoyama, A., Johns, W.D., 1971, Catalytic conversion of fatty acids to petroleum-like paraffins and their maturation: Nature (Phys. Sci.), v. 232, p. 140-144.
- Silverman, S.R., and Epstein, S., 1958, Carbon isotopic compositions of petroleum and other sedimentary organic materials: Amer. Assoc. Petroleum Geologists Bull., p. 998-1012.
- Smith, P.V., 1954, Studies on origin of petroleum: occurrence of hydrocarbons in recent sediments: Amer. Assoc. Petroleum Geologists Bull., v. 38, no. 3, p. 377-404.

- Souza, N.J., and Nes, W.R., 1968, Sterols: isolation from a Blue-Green alga: *Science*, v. 162, p. 363.
- Spears, A.W., Lassiter, C.W., and Bell, J.H., 1963, Quantitative determination of hydrocarbons in cigarette smoke: *Journal of Gas Chromatography*, p. 34-37.
- Speziale, M.H., 1972, Correlation of hydrocarbons in shales and oil, Peoria field, Colorado: M. Sc. Thesis, Colorado School of Mines, T-1444, 68 pp.
- Stevens, N.P., 1956, Origin of petroleum, a review: *Amer. Assoc. Petroleum Geologists*, v. 40, no. 1, p. 51-61.
- \_\_\_\_\_, Bray, E.E., and Evans, E.D., 1956, Hydrocarbons in sediments of Gulf of Mexico: *Amer. Assoc. Petroleum Geologists*, v. 40, no. 5, p. 975-983.
- Streibl, M., and Herout, V., 1969, Terpenoids in Eglinton, G., and Murphy., *Organic Geochemistry Methods and Results*: Springer-Verlag, New York - Heidelberg - Berlin.
- Waples, D.W., 1972, Catalytic formation of hydrocarbons from fatty acids: *Nature (Phys. Sci.)*, v. 323, p. 140-144.
- Welte, D.H., and Ehardt, G., 1968, Distribution of long-chain n-paraffins and n-fatty acids in sediments from the Persian Gulf: *Geochim. Cosmochim. Acta*, v. 32, p. 465-466.