

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY, GEOCHEMISTRY
AND PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
SEATTLE MEETING, MARCH 20-25, 1983

BIOMARKERS IN OIL SHALE: OCCURRENCE AND APPLICATIONS

By

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INTRODUCTION

Biological markers, compounds derived essentially unchanged from living organisms, have been used by petroleum geologists to relate oils to their original source rock material (1, 2). This technique is based on the ubiquitous nature of biomarkers in ancient sediments and on the characteristic way in which ratios of biomarkers vary from location to location.

We are extending this technique to the oil shale industry by determining biomarker ratios in oils produced from Green River formation shales and by studying the manner in which these ratios vary with depth and other characteristics of the shale within a given core.

Past work on the biomarkers in oil shale has involved characterization of the biomarkers in bitumen, the soluble organic portion of oil shale and determination of the manner in which their quantity varied with depth in relation to other hydrocarbon types (3, 4). Biomarker derivatives from kerogen, the insoluble organic portion of oil shale, have been determined by a variety of methods (5) and compared to their bitumen analogs (6, 7, 8). Since not all the biomarker compounds from a given shale sample occur in the same proportions in both the bitumen and the oil and since heat treatment is involved in commercial oil production, we have evaluated biomarker occurrence in the whole oil product prepared at a heating schedule comparable to the standard assay procedure (12°C/min, maximum 500°C). We previously established that the biomarkers from kerogen occur in the oil as both unsaturated and saturated compounds (ene and ane) and although the ratios of ene/ane vary with heating rate, the sums of ene plus ane ratios are fairly constant (9). This is important in validating the use of biomarker ratios in oils produced at widely varying heating rates (geological, in-situ retorting, assay, very rapid pyrolysis).

In this work, we have prepared oils from cores in varying locations in the Green River formation in order to compare biomarker ratio characteristics that correlate across the resource, as well as the factors that distinguish one location from another. Beside being of diagnostic value for oil shale retorts, this information provides possible insights into the geochemistry of oil shale and the structure of kerogen and bitumen.

EXPERIMENTAL

Samples

Oil shale core samples were available from two widely separated (East, West) locations in the Green River formation. The first core we studied was from the Geokinetics site near Vernal, Utah. In this area, the Mahogany zone is close to the surface and less than 50 feet thick. Oils were prepared from 1-foot composite samples spanning 45 to 85 feet in depth. These samples had been previously prepared at our laboratory (-20 mesh) and elemental analyses for total carbon, mineral carbon, hydrogen, nitrogen and sulfur were complete. Grade was calculated using a correlation established at our laboratory (10) between organic carbon content and grade that has a standard error of 0.56 gal/ton. These samples varied in grade from 4.05 to 52.30 gal/ton. Geokinetics' designation for this core is "Exp. 22" and they locate the Mahogany Marker at 47.6 feet and the Mahogany Bed at 53.2 feet (11).

The second core we have completed analyzing is Naval Oil Shale Reserve (NOSR) Core 25 from the Anvil Points area near Parachute Creek, Colorado. These shale samples were prepared for a comprehensive study by Giaque et al. (12) and were the consistency of fine talc. Their grade had been determined (at LETC) by the ASTM standard method and varied from 1.95 to 56.50 gal/ton. We prepared oils from 1- and 2-foot composites ranging in depth of burial from 623 to 702 feet. The Mahogany Marker is estimated from the grade variation to occur close to 664 feet. The A-groove, which occurs from approximately 630 to 640 feet, was included in this core, but not in the Geokinetics core. NOSR Core 15/16 from the same source is currently being analyzed and its data will be available shortly.

Procedure

Ten Oil Shale Samples (TOSS) were simultaneously pyrolyzed in a segmented reactor constructed of stainless steel (Figure 1). Approximately 12 g of shale was weighed into each 6-inch high individual sample vessel with stainless steel frit bottom. The vessels were placed into the 10 compartments of the reactor resting on a wire mesh so as to be positioned near the center of the furnace. The lid with 3 thermocouples and a gas inlet was bolted into place with a Viton O-ring seal (the top flange was positioned just outside the furnace). The charged reactor was placed in a 3-zone furnace and the samples were heated at about 10°C/min up to 500°C where the temperature was held for 30 minutes. An argon flow was maintained throughout the experiment to aid in removing vapors from the reactor and to minimize their residence time in the hot zone. Oils were collected in individual U-shaped glass tubes packed with glasswool and immersed in an ice bath. Noncondensable gases were vented through a common manifold and exit line containing a flowmeter.

Chromatography

In order to avoid problems with sample inhomogeneity, the entire oil sample from each sample of shale was dissolved in 1.5 to 2.5 mL of CS₂ (about 1 g oil to 1.5 mL solvent). One μ L of this solution was injected into a Hewlett-Packard Model 5880 Gas Chromatograph equipped with capillary inlet and a 50 m x 0.25 mm Quadrex "007" methyl silicone column. Injection on the column is made with a split ratio of approximately 1 to 100. The column temperature started at 60°C and increased at 4°C/min to 280°C where it remained for a total run time of 90 min. The carrier gas was helium at a pressure of 0.27 MPa flowing at a rate of 1 cm³/min. The injector temperature was 325°C and the flame ionization detector (FID) temperature was 350°C. Data reduction was done using a Hewlett-Packard Model 3354 Laboratory Automation System with a standard loop interface. Identification of various components was based on GC/MS interpretation described previously (9).

Data Analysis

A list of the ratios calculated from the chromatograms are given in Table I. By cores, these ratios for the individual oils were entered into a data file which also included depth of burial, grade and elemental nitrogen/organic carbon of the raw shale. Using computer codes available on an LLNL CDC-7600 (CRSCOR and CROSSPLOT2), we were able to calculate cross-correlation coefficients for all pairs of variables and to plot various data pairs.

RESULTS AND DISCUSSION

We have investigated the variations in two groups of biomarker compounds, chain isoprenoids and steranes, in gas chromatograms of oils produced from two Green River formation cores. The chain isoprenoids ranged from 14 to 20 carbons in size and included several alkene forms. The three steranes we tentatively identified are the tetracycloalkanes, α - and β -ergostane and a stigmastane isomer. We also measured the ratios of normal alkenes to alkanes and the odd/even carbon preference for comparison purposes.

For the Geokinetics core, we prepared 38 oils at 1-foot composites and for NOSR Core 25 we prepared 43 oils at 1- and 2-foot composites. Since the NOSR core included the A-groove immediately above the Mahogany zone, we have used only the 28 samples from the Mahogany zone (600 to 702 feet) in some comparisons, to look for any differences resulting from its inclusion. The C₁₇ odd/even ratio, elemental nitrogen/organic carbon ratio and several biomarker ratios were considerably higher in the A-groove than anywhere in the Mahogany zone.

There has been considerable speculation about the source material responsible for biomarker compounds in oil shale and about the effect of deposition and aging conditions on their distribution (13-17). We are here concerned with the variation in relative amounts of biomarkers with stratigraphy in oils from the Mahogany zone and with the possible application of this information to the commercial development of the resource. At the same time, we have looked at the relationship of biomarkers to other variations in the shale and to the geochemistry of the resource.

Biomarker compounds are present in varying proportions in both the bitumen and kerogen of oil shale, the non-bitumen forms being chemically bound or physically trapped by the kerogen and mineral matrix (9, 18). Burnham et al. (9) observed that the ene/ane ratios of several chain isoprenoid compounds in shale oil behaved like the n-alkanes, e.g., ratios of ene/ane varied over a wide range of heating rates, but sums of ene plus ane were approximately constant. Since pyrolysis of kerogen results in production of both the saturated (ane) and unsaturated (ene) forms of n-alkanes and chain isoprenoids, with ene/ane ratios increasing at varying rates for each compound with increasing heating rate, we have reported some of our ratios as the sums of the ene and ane forms. Phytane, which occurs mainly in bitumen, was an exception for which no unsaturated form was found. Therefore, the ene/ane ratios in shale oil are affected by the severity of the heat treatment and by the distribution of biomarkers between bitumen and kerogen in the raw shale. Based

on these observations we can extrapolate with confidence from high heating rates to very slow ones by using ratios of the ene plus ane forms of the alkanes and biomarkers. In our laboratory, we have found that this relationship applies over a wide range of conditions including very rapid pyrolysis in a fluidized bed and very slow pyrolysis at high pressures (19, 20).

TABLE I

RATIOS CALCULATED FROM THE GC PEAKS FOR EACH OIL SAMPLE

C_8 through C_{28} straight chain hydrocarbons:	1-alkene/alkane
C_{11} through C_{29} straight chain hydrocarbons:	odd/even ratios*
Pristane/ C_{17} 's + C_{18} 's	(2,6,10,14-tetramethylpentadecane, C_{19})
Prist-1-ene/ C_{17} 's + C_{18} 's	
Prist-2-ene/ C_{17} 's + C_{18} 's	
Pristane + 1-ene + 2-ene/ C_{17} 's + C_{18} 's	
Phytane/ C_{18} 's + C_{19} 's	(2,6,10,14-tetramethylhexadecane, C_{20})
Phytane/Pristane	
Phytane/Pristane + 1-ene + 2-ene	
Phytane/Prist-2-ene	
Phytane/Prist-1-ene	
2,6,10-trimethyldodec-1-ene/ C_{13} 's + C_{14} 's	(1-ene of farnesane)
Farnesane/ C_{13} 's + C_{14} 's	(2,6,10-trimethyldodecane, C_{15})
2,6,10-trimethyldodec-1-ene/Farnesane	
2,6,10-trimethyldodec-1-ene + Farnesane/ C_{13} 's + C_{14} 's	
2-6,10-trimethylundec-2-ene/ C_{13} 's	
2,6,10-trimethyltridec-1-ene/ C_{13} 's + C_{14} 's	
2,6,10-trimethyltridecane/ C_{14} 's + C_{15} 's	
2,6,10-trimethyltridecane + 1-ene/ C_{14} 's + C_{15} 's	
β -ergostane/ C_{29} 's + C_{30} 's,	($C_{28}H_{50}$)
α -ergostane/ C_{29} 's + C_{30} 's	($C_{28}H_{50}$)
stigmastane/ C_{30} 's,	($C_{29}H_{52}$)

Note: C_{17} 's implies the sum of the 1-alkene + alkane of the normal C_{17} hydrocarbon, etc.

* Odd/even ratios were calculated with the formula:

$$\frac{2 \times (C_{\text{odd}} \text{ alkene} + \text{alkane})}{(C_{\text{odd}-1} \text{ alkene} + \text{alkane}) + (C_{\text{odd}+1} \text{ alkene} + \text{alkane})}$$

Although the two cores in this study were located across the formation from each other, we found there was very good agreement between the average values for odd/even preferences (Figure 2) and alkene/alkane ratios (Figure 3) vs carbon number. This demonstrates a consistency in the average values for these ratios in Mahogany zone oils. Another comparison between the two cores is presented in Table II based on biomarker ratios. We find that the average values agree very well for the two cores with the exception of the steranes which are appreciably higher in the NOSR core. This is true even when the A-groove data is excluded.

The ratios of pristane compounds (ane, 1-ene, 2-ene) to phytane are of interest since pristane/phytane ratios in bitumen and/or kerogen are often cited as indicators of terrestrial/laquestrine source material (1-3). Prist-1-ene from kerogens and sediments have been linked to a common precursor of pristane and phytane (21, 22). Anders and Robinson (3) report pristane/phytane ratios averaging 0.44 in Green River formation bitumens. However, these ratios are not indicative of the whole shale oil ratios because most of the phytane comes from the bitumen and most of the pristane compounds are produced from the kerogen. Connan and Cassou (16) discuss pristane/phytane ratios in a variety of crude oils and conclude that ratios lower than 1.5 are indicative of oils derived from "marine shale--carbonate sequences" while ratios greater than 3.0 indicate a significant amount of terrestrial source material. These crude oil ratios are probably more valid

for comparison to whole shale oil samples than are the bitumen ratios. Including the three pristane forms in the ratio of pristane+1-ene+2-ene/phytane gives us values indicative of small, but significant and highly variable terrestrial input at differing levels within each core. The pristane/phytane ratios varied from 0.52 to 1.33 (average 0.78) in the Geokinetics core and from 0.40 to 1.14 (average 0.58) in the NOSR core, while pristane+1-ene+2-ene/phytane ratios varied from 1.54 to 4.35 (average 2.78) and from 1.61 to 5.26 (average 2.63), respectively. It is interesting to note that although these two cores are located near the opposite boundaries of the resource, the ranges and averages for these ratios are nearly the same. However, the maxima and minima do not appear to correspond to the same strata.

TABLE II

COMPARISON OF BIOMARKER RATIOS IN TWO GREEN RIVER FORMATION CORES

Biomarker Ratio*	NOSR Core 25						
	Geokinetics Core			with			
	Min.	Max.	Avg.	Min.	Max.	A-groove Avg.	without A-groove Avg.
pristane	0.09	0.55	0.21	0.03	0.38	0.15	0.16
prist-1-ene	0.15	0.76	0.40	0.13	1.03	0.39	0.39
prist-2-ene	0.05	0.31	0.14	0.04	0.30	0.11	0.10
pristane + 1-ene + 2-ene	0.30	1.22	0.75	0.21	1.62	0.66	0.65
phytane	0.08	0.90	0.29	0.06	0.59	0.28	0.28
prist-1-ene/phytane	0.52	2.63	1.41	0.83	3.13	1.49	1.41
prist-2-ene/phytane	0.26	1.00	0.48	0.20	1.64	0.40	0.35
pristane + 1-ene + 2-ene/phytane	1.54	4.35	2.78	1.61	5.26	2.63	2.33
pristane/phytane	0.52	1.33	0.78	0.40	1.14	0.58	0.56
trimethyldodec-1-ene	0.01	0.19	0.10	0.04	0.25	0.11	0.11
farnesane	0.06	0.20	0.13	0.05	0.29	0.13	0.13
trimethyldodec-1-ene/farnesane	0.55	1.07	0.78	0.47	1.26	0.82	0.80
trimethyldodec-1-ene + farnesane	0.11	0.38	0.22	0.10	0.54	0.25	0.23
trimethylundec-2-ene	0.15	0.47	0.31	0.19	1.07	0.44	0.41
trimethyltridec-1-ene	0.06	0.22	0.14	0.06	0.45	0.20	0.18
trimethyltridecane	0.03	0.37	0.20	0.08	0.56	0.24	0.22
trimethyltridecane + 1-ene	0.16	0.59	0.35	0.14	1.00	0.44	0.41
β -ergostane	0.02	0.26	0.10	0.05	0.69	0.23	0.20
α -ergostane	0.02	0.39	0.12	0.01	1.54	0.27	0.20
?=stigmastane	0.19	1.68	0.65	0.25	5.91	1.56	1.35

* Values reported are for ratios of biomarkers to the respective alkene plus alkanes as expressed in Table I.

The overall prist-1-ene content of the oil is markedly higher than the pristane or prist-2-ene for both cores. It has been suggested that prist-1-ene is related to a kerogen precursor of the pristane and phytane in bitumen (14). Although the correlations are not particularly strong for prist-1-ene vs N/C_{org} (- .10, -.24) and prist-2-ene vs N/C_{org} (+ .37, + .69) in the two cores, they are opposite in sign and, thus, may indicate a difference in source material or production mechanism. The unravelling of this relationship will require further work. It is noteworthy that both van de Meent and Larter found prist-1-ene to be present in pyrolysis products from a large variety of kerogens (15, 21).

Both grade and nitrogen/organic carbon atomic ratio in the raw shale vary characteristically with depth in the two cores (Figures 4 and 5) through the Mahogany zone. The A-groove in NOSR Core 25 has the maximum $N/Org.C$ ratio (.24) as well as the leanest shale material (1.65 gal/ton). This inverse relationship between grade and $N/Org.C$ has been noted previously (10). The occurrence of maximum $C_{17}odd/even$ ratio is very pronounced in this region of high $N/Org.C$, as are some of the biomarker compounds (Figure 6).

The depth profiles of three types of compounds studied are given in Figures 6 and 7 and indicate the variation observed in these ratios throughout the two cores. Their behavior is similar at some levels and not at others which would be expected given the complicating factors of natural phenomena at work over geologic time periods.

The cross-correlation coefficients for all pairs of biomarker ratios odd/even ratios, ene/ane ratios, shale grade, $N/Org.C$ and depth were calculated for each core separately. A selection from these data is presented in Table III for comparison of the behavior of biomarkers relative to

each other and to shale properties. This is a very abbreviated list of the cross-correlation data and represents the best correlations in some cases or those with special significance. There was no consistent correlation of biomarkers in both cores with grade or depth over the ranges investigated.

TABLE III
CORRELATION COEFFICIENTS FOR SELECTED VARIABLE PAIRS

Variable 1*	Variable 2*	Coefficient, r		
		Geokinetics core	NOSR with A-groove	Core 25 without A-groove
phytane	pristane	0.90	0.83	0.90
phytane	trimethylundec-2-ene	0.66	0.80	0.64
phytane	farnesane	0.65	0.80	0.61
phytane	trimethyltridecane	0.71	0.79	0.59
phytane	pristane + 1-ene + 2-ene	0.67	0.79	0.85
pristane + 1-ene + 2-ene	trimethylundec-2-ene	0.84	0.84	0.89
pristane + 1-ene + 2-ene	farnesane	0.88	0.81	0.86
pristane + 1-ene + 2-ene	trimethyltridecane	0.64	0.81	0.82
farnesane + 1-ene	trimethyltridecane + 1-ene	0.84	0.95	0.91
farnesane + 1-ene	trimethylundec-2-ene	0.85	0.91	0.84
farnesane + 1-ene	α -ergostane	0.37	0.82	0.62
trimethyltridecane + 1-ene	trimethylundec-2-ene	0.78	0.92	0.87
trimethyltridecane + 1-ene	α -ergostane	0.46	0.79	0.56
trimethyltridecane + 1-ene	β -ergostane	0.22	0.77	0.74
α -ergostane	stigmastane	0.78	0.80	0.89
α -ergostane	β -ergostane	0.23	0.72	0.86
β -ergostane	stigmastane	0.39	0.78	0.82
N/org. carbon	C ₁₇ odd/even	0.54	0.88	0.47
N/org. carbon	prist-2-ene	0.37	0.69	0.23
N/org. carbon	prist-1-ene	-0.10	-0.24	-0.20
N/org. carbon	α -ergostane	0.52	0.58	0.57
C ₁₉ odd/even	trimethyltridecane	0.57	0.77	0.76
C ₁₉ odd/even	phytane	0.50	0.69	0.69
C ₂₇ odd/even	α -ergostane	0.55	0.29	0.61
C ₁₇ odd/even	α -ergostane	0.53	0.62	0.58

* Values reported are for ratios of biomarkers to the respective alkene plus alkanes as expressed in Table I.

In general, the correlations were higher in the NOSR core than in the Geokinetics core data. This was especially evident for the sterane compound correlations and, in particular, the β -ergostane which in the Geokinetics core did not correlate significantly with either of the other two steranes. The reason for this is not evident, but may be due to the fact that the peak is quite small and obscured by nearby peaks. However, there was good correlation in both cores between the following pairs: phytane and pristane, pristane and trimethylundecene, pristane and farnesane, farnesane and trimethyltridecane, farnesane and trimethylundecene, trimethyltridecane and trimethylundecene, stigmastane and α -ergostane. This consistency of correlation among like groups of biomarkers was also observed by Anders and Robinson. It may indicate separate source materials for the chain isoprenoids and the steranes and/or it may indicate a series of degradation products from a different precursor for each group.

The data and discussion presented here are still of a tentative nature, since work on a third core is currently in progress. We anticipate further clarification of the behavior of biomarkers in oil shale with this expanded data base.

CONCLUSIONS

We investigated some biomarkers present in oils produced from two Green River formation cores using capillary column gas chromatography and found strong correlations between chain

isoprenoid compounds and between two of the sterane compounds in both cores. The biomarker compounds showed measurable changes in their ratios to associated alkanes with stratigraphy, thus, supporting the validity of relating shale oils to their source rocks using biomarker ratios. The problem of relating time dependent process variables to an oil product, subject to indefinite migration times through an in-situ-retort, may be resolved with biomarker tracers.

Comparison of these two Green River formation cores shows good agreement in ranges and average values for the alkene/alkane ratios and odd/even ratios of normal hydrocarbons across the resource. Of the two groups of biomarker compounds studied, the chain isoprenoids showed better agreement in ranges and averages than the steranes in the two-core comparison. The maximum variations in ratios of all three groups of compounds occur near the Mahogany marker in both cores and in the NOSR core again near the top of the A-groove. The relationship of variations in these biomarker ratios in oil to other properties of the oil shale source material could provide a better understanding of the structure and geochemistry of kerogen.

ACKNOWLEDGMENTS

We wish to thank Stanley Grotch for help and assistance with the data analysis and Cal Hall and Jim Taylor for mechanical technician support. We also thank Carla Wong and Richard Crawford who identified the steranes by GC/MS and Jane Cupps who helped with the gas chromatography. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

EXPERIMENTAL APPARATUS

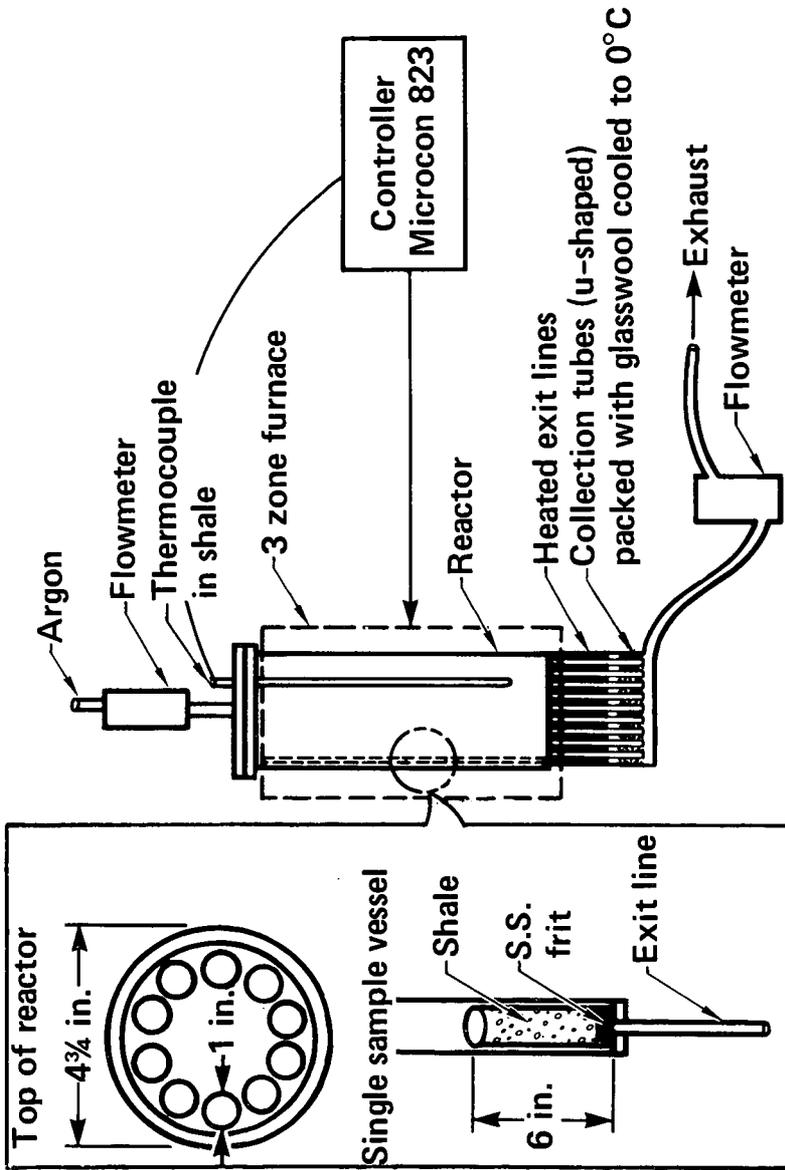


Figure 1. TOSS apparatus for producing oil from ten oil shales simultaneously.

**AVERAGE N-ALKANE + ALKENE ODD/EVEN RATIO
vs CARBON NUMBER**

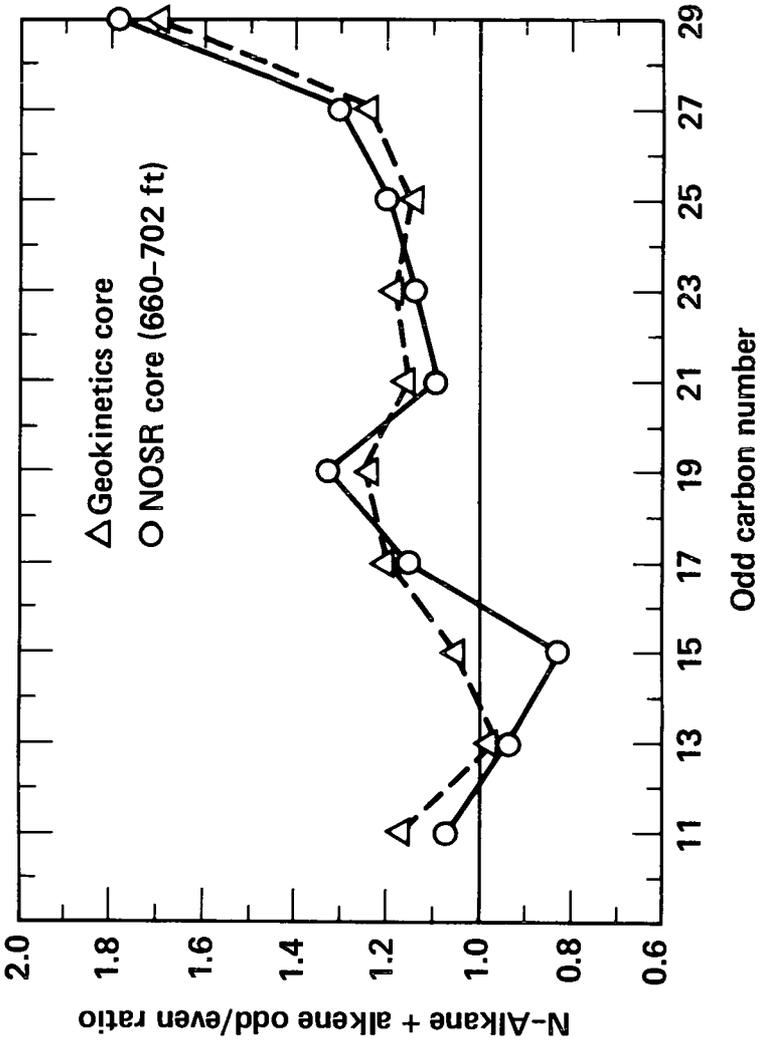


Figure 2. Plot of the average normal alkane + alkene odd/even ratios versus carbon number in the Geokinetics core and NOSR Core 25.

**AVERAGE 1-ALKENE/N-ALKANE RATIO
vs CARBON NUMBER**

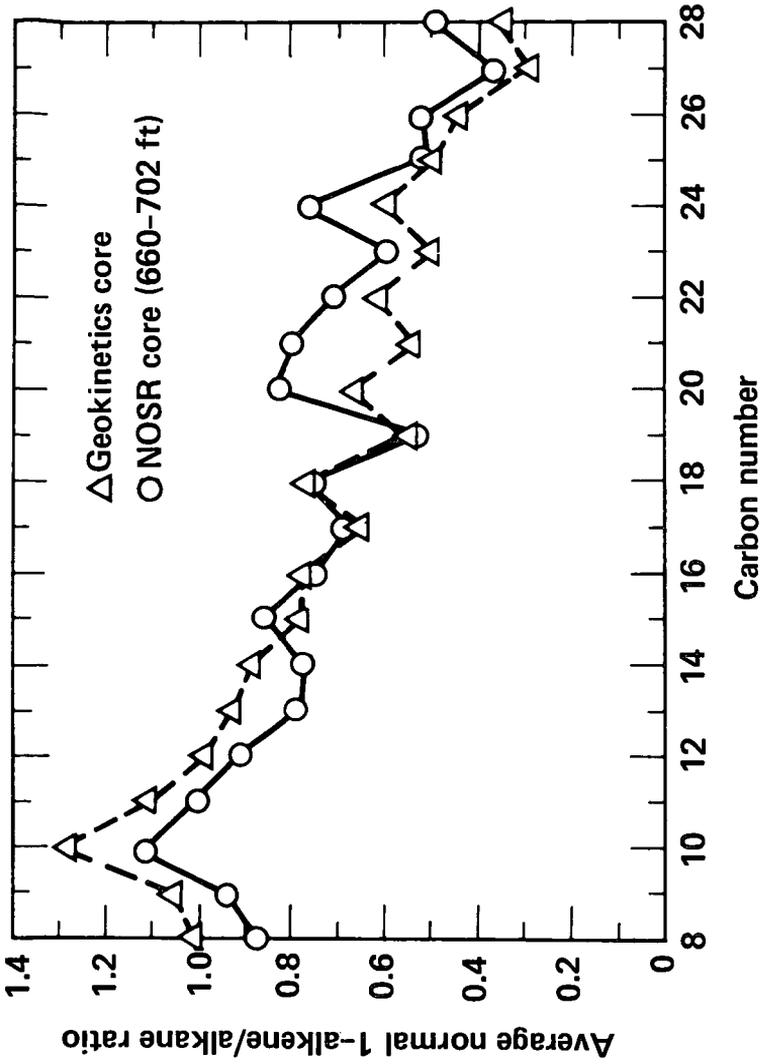


Figure 3. Plot of the average 1-alkene/normal alkane ratios versus carbon number in the Geokinetics core and NOSR Core 25.

**SHALE GRADE AND NITROGEN/ORGANIC CARBON RATIO vs
DEPTH (NOSR CORE 25)**

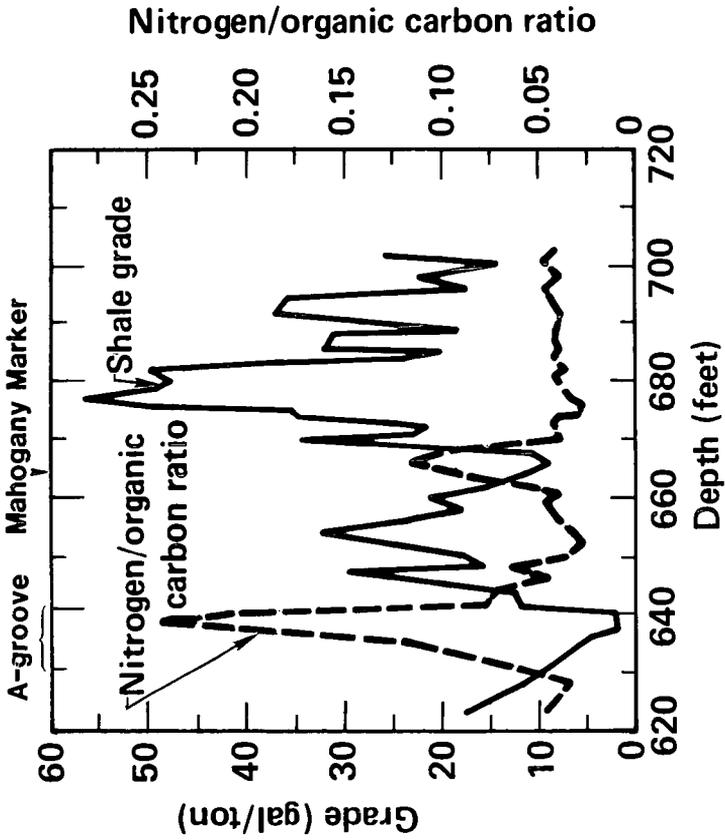


Figure 4. Plot of shale grade and nitrogen/organic carbon ratio versus depth in NOSR Core 25.

SHALE GRADE AND NITROGEN/ORGANIC CARBON RATIO vs
DEPTH (GEOKINETICS)

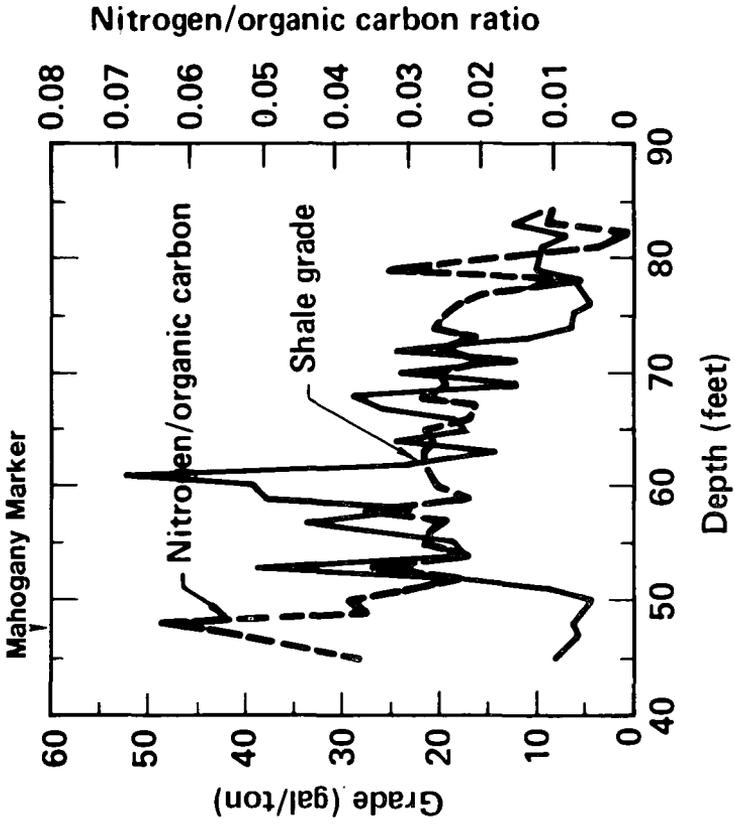


Figure 5. Plot of shale grade and nitrogen/organic carbon ratio versus depth in Geokinetics core.

BIOMARKERS vs DEPTH (NOSR CORE 25)

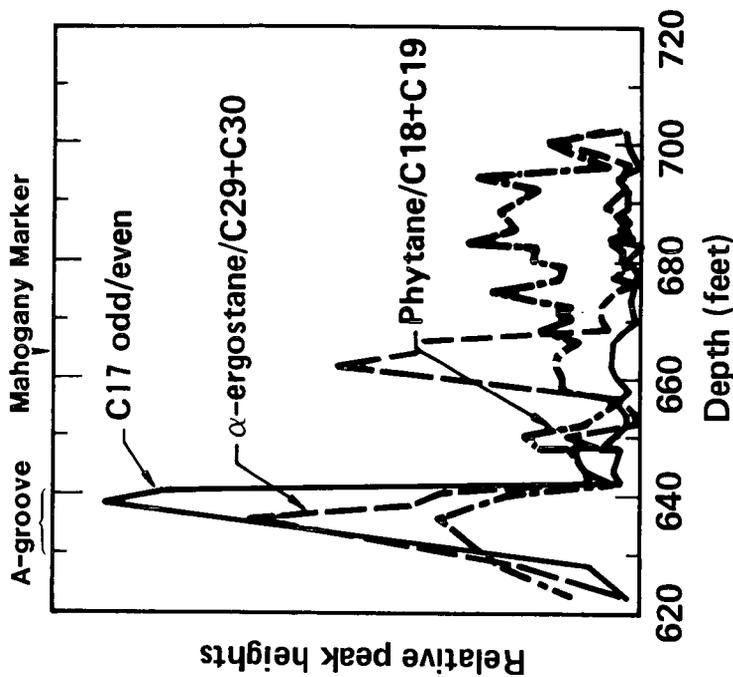


Figure 6. Plot of biomarker compounds versus depth in NOSR Core 25.

BIOMARKERS vs DEPTH (GEOKINETICS)

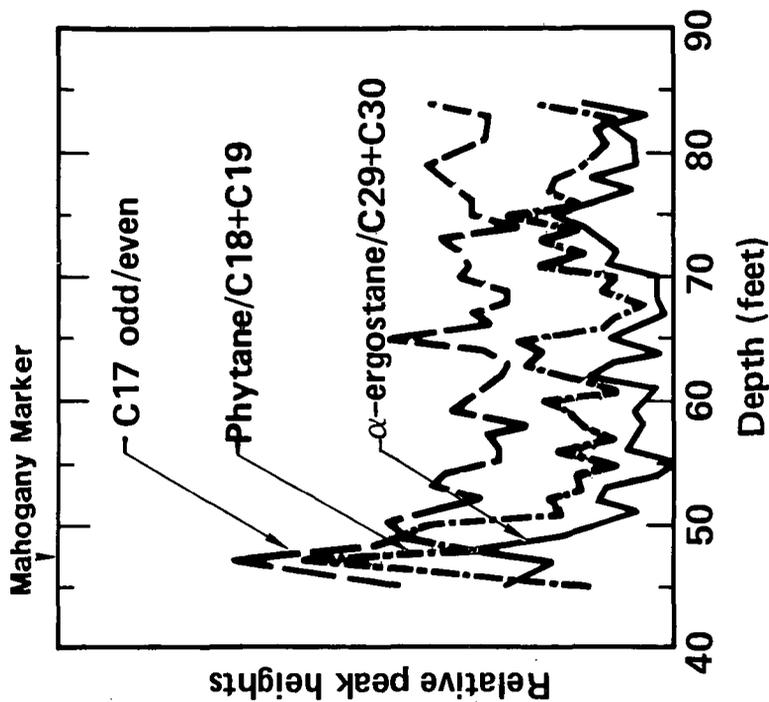


Figure 7. Plot of biomarker compounds versus depth in Geokinetics core.

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