CHARACTERIZATION AND GEOCHEMISTRY OF DEVONIAN OIL SHALE NORTH ALABAMA - SOUTH CENTRAL TENNESSEE

By

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INTRODUCTION

For the past three years, the Geological Survey of Alabama, in cooperation with the U. S. Department of Energy, has conducted a regional oil shale resource assessment of the Chattanooga Shale in north Alabama, northwest Georgia and south-central Tennessee (Figure 1). The work has involved an extensive outcrop sampling program, a limited drilling program in Alabama for subsurface data and a program to determine the physiochemical properties of the oil shale, and to analyze the shale for a series of trace metals of possible commercial value or environmental hazard.

Results from this study have delineated a four-county area in north Alabama and south-central Tennessee as having the best oil potential of the Devonian Chattanooga Shale in the southernmost part of the Highland Rim section. These four counties, Limestone and Madison Counties, Alabama, and Giles and Lincoln Counties, Tennessee, have an average oil yield of 13.9 gallons per ton (gal/t) with a maximum value of 23.9 gal/t. Within this area, more than 45 outcrops were sampled on 2 foot intervals upward from the lower contact of the shale. A limited drilling program of nine core holes provided 388 feet of shale, which were sampled at 2 foot increments or at distinct lithologic changes (1, 2).

GEOLOGIC SETTING

The Chattanooga Shale of Late Devonian age occurs on the surface and in the subsurface over almost all of the regional study area. The general outcrop line of the shale is shown in Figure 1.

In northern Tennessee, the Chattanooga Shale is subdivided into the upper Gassaway Member, the lower Dowelltown Member, with the Hardin Sandstone at the base. In Alabama, Georgia and south-central Tennessee, only the upper Gassaway Member appears to be present.

Stratigraphically, the Chattanooga Shale unconformably overlies Ordovician or Silurian age sandstone, shale and limestone and itself is overlain with local disconformity by the Maury Formation of Late Devonian to Early Mississippian age or by the Early Mississippian Fort Payne Chert.

Surface exposures of the Chattanooga Shale thicken away from the margin of the Highland Rim towards the fold belt provinces to the east and into the Warrior Basin on the south-southwest, with 82 feet of Chattanooga Shale recorded from a deep test well in northern Greene County, Alabama.

Depositional environment of the Chattanooga Shale was clearly marine, as indicated by the presence of marine fossils including brachiopods and conodonts and the local occurrence of phosphate. Generally high V:Ni ratios in the extracted oil also help substantiate a marine deposition for this shale. Deposition of the shale was apparently irregular, since it may vary greatly in thickness and lithologic composition between adjacent outcrops and is absent over pre-Chattanooga structural highs.

CHARACTERIZATION AND GEOCHEMISTRY

Mineralogy

In hand specimen, the Chattanooga Shale is typically a dark grey to black, organic, pyritiferous, marine shale with thin lenses and interbeds of sandstone, siltstone and silty shale. Phosphate nodules and cherty layers occur locally. Rock slabs cut from drill cores show the distinctive dark color of the shale, the thin discontinuous siltstone laminae, thin pyrite laminae and typical elongate pyrite blebs.

The characteristic black color is derived primarily from hydrogen-rich (H/C = 1.42) sapropelic matter apparently derived from algae and lesser amounts of spores and pollen. In outcrop,

the silt laminae appear to weather slightly faster than the clay laminae, imparting a finely fissile character to the shale. Freshly broken shale samples typically emit a strong, petroliferous odor. Locally samples from highly petroliferous zones will support combustion and have been used for heating fuel.

Mineralogically, the Chattanooga Shale is composed of 22% organic matter (kerogen), 31% clay minerals (illite and kaolinite), 22% quartz, 9% feldspars and 11% pyrite and marcasite. Accessory minerals such as calcite, apatite, tourmaline and zircon are also known to occur. In thin section, the kerogen occurs as coatings on the larger mineral grains as well as stringlike concentrations and globules along laminae.

X-Ray diffraction analyses show little mineralogical variation between shale samples. Detailed X-ray analysis of the shale interval from one of the core holes indicates the following mineralogy: chlorite, illite, feldspar, kaolinite, quartz, pyrite, calcite and dolomite. A series of X-ray diffractograms of 1-foot increments of shale from one of the cored intervals suggest that some minor vertical mineralogical changes occur within the interval (Figure 2). In general, there is an increase in calcite and dolomite and a decrease in the pyrite content from top to bottom.

Shale samples from the core hole were also analyzed for mineral composition using a scanning electron microscope (SEM). Uncoated square cut shale samples were mounted on aluminum stubs with silver paint and stored in a desiccator under vacuum until placed in the SEM. The SEM analyses were performed on an Etec-Auto Scan unit worked at 20 kilovolts. SEM mineral identifications are based on visual comparisons to standard reference images. Identifications have not been confirmed by microprobe analysis. Typical images observed are shown in Figure 3.

Figure 3A shows a dickite grain; a well-crystallized member of the kaolin group encased in a matrix of mixed-layered clays. Figure 3B shows pyrite occurring as closely packed clusters of pyritohedrons common to almost all of the scanned shale samples. Well structured sheets of kaolinite (Figure 3C) are also commonly observed associated with the undifferentiated mixed-layered clays. Amorphous appearing irregularly shaped zones of material (Figure 3D) are intimately associated with the mixed-layered clays and are interpreted to be organic matter. Other minerals identified using SEM include illite, halloysite, quartz and feldspar.

Fischer Assay

Shale samples collected from surface exposures and core samples from the drilling program were crushed and sized to produce representative 500 gram samples. All samples were submitted for analysis of shale oil content by modified Fischer Assay methods. Assays were performed at the Colorado School of Mines and the Alabama Mineral Research Institute. Average oil yields for samples in the four-county area range from 6.9 to 19.2 gal/t (Table I).

Whole Rock and Trace Metal Geochemistry

Chemical characterization of the Chattanooga Shale involved whole rock and trace metal analyses on shale samples having more than 7 gal/t oil yield from the four-county area. These analyses were done to ascertain the chemical character of the spent shale as it might affect the environment or add to the economic process.

Preliminary whole rock analyses of samples from 42 shale sections indicate an average shale composition of 43.33% SiO_2, 11.60% Al_2O_3 and 9.79% Fe_2O_3, with minor amounts of MgO, CaO, MnO, Na_2O, K_2O, TiO_2 and P_2O_5 (Table II). These analyses compare favorably to analyses of other Devonian organic shales, but the Chattanooga Shale samples of north Alabama and south-central Tennessee are anomalously lower in silica and higher in iron and titanium (Table III).

Ultimate and proximate analyses were also run on all shale samples having more than 7 gal/t oil. Average values are 1.12% moisture, 72.60% ash, 16.59% volatiles, 9.85% fixed carbon and 2,765 BTU's. Average elemental composition of the 42 sampled sections is 16.08% total carbon, 0.50% nitrogen, 6.57% sulfur, 1.85% hydrogen and 2.91% oxygen.

Trace metals examined during the characterization study include cobalt, chromium, molybdenum, nickel, vanadium and zinc. Uranium determinations were also made on each sample as part of evaluating the full energy resource potential of the shale (3). Average trace metal contents and value ranges for 42 shale sections analyzed are given in Table III.

Organic Geochemistry

Rock eval pyrolysis analyses were made on nine samples of 13 gal/t plus rock from five locations within the study area (Table IV). Average total organic carbon content for the nine samples is 16.27 wt. % with an average hydrogen index of 323 mg hydrocarbon (HC)/g of organic carbon at an average pyrolysis temperature of 423°C. Free hydrocarbon averages 2.33 mg/g of rock for the nine samples, with an average residual hydrocarbon potential of 52.58 mg/g of rock. CO_2 produced from the kerogen pyrolysis is approximately 3.67 mg/g of rock for these samples.

The hydrocarbon fractions of five samples from three locations within the study area were also analyzed. Saturated hydrocarbon analyses average 5.2% paraffin, 0.80% isoprenoid and 94%

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naphthene (Table V). Average composition of the extracted oil is 7.2% paraffins–naphthenes, 25.6% aromatics, 6.0% sulfur, 41.0% precipitated asphaltene, 16.8% eluted NSO's and 3.6% non–eluted NSO's (Table VI).

TABLE I

SAMPLE LOCATIONS AND AVERAGE OIL YIELD PER SAMPLE FOR CHATTANOOGA SHALE
IN LIMESTONE AND MADISON COUNTIES, ALABAMA, AND
GILES AND LINCOLN COUNTIES, TENNESSEE

Sample Number	Oil Yield (g/t)	Sample Number	Oil Yield (g/t)
LIM–1	11.1	GIL–10	19.2
LIM–2	9.8	GIL–11	15.7
LIM–3	15.5	GIL–12	15.7
LIM–4	13.1	GIL–13	14.7
LIM–5	11.5	GIL–14	14.8
MAD–1	10.4	GIL–15	15.5
MAD–2	11.9	LIN–1	19.2
MAD–3	8.7	LIN–2	14.2
MAD–5	14.3	LIN–3	12.0
MAD–6	11.6	LIN–4	9.7
MAD–7	12.0	LIN–5	6.9
MAD–8	11.9	LIN–6	16.5
GIL–1	15.5	LIN–7	16.7
GIL–2	18.2	LIN–8	16.9
GIL–3	19.2	LIN–9	11.3
GIL–4	14.3	LIN–10	11.5
GIL–5	15.6	LIN–11	14.7
GIL–6	15.2	LIN–12	11.0
GIL–7	16.6	LIN–13	14.5
GIL–8	14.8	LIN–14	13.6
GIL–9	11.5	LIN–15	12.1

TABLE II

WHOLE ROCK ANALYSES OF DEVONIAN SHALES (1, 6-9)

	AL	WV	WV	TX	TN	OH
			(percent)			
SiO_2	43.33	56.92	58.39	50.3	49.30	60.65
Al_2O_3	11.60	16.42	16.50	4.6	10.71	11.62
Fe_2O_3	9.79	6.58	6.45	10.0	9.60	.36
MgO	1.61	1.54	1.70	2.6	1.22	1.90
CaO	.95	1.43	.82	7.4	.36	1.44
MnO	.02	.05	--	--	--	.04
Na_2O	.49	.68	.47	.29	.33	.60
K_2O	3.98	3.65	3.83	1.6	4.03	3.10
TiO_2	1.26	.72	.70	--	.69	.62
P_2O_5	.25	.01	.14	--	.12	.18
LOI	26.81	--	--	--	23.0	19.01

A gas chromatograph of the C_{15+} fraction of the saturated hydrocarbon component indicates that the major compound distribution, C_{15} to C_{20}, makes up 68.9% of the total fraction

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(Figure 4).

TABLE III

TRACE ELEMENTS IN DEVONIAN SHALE (1, 7, 10)

		Alabama		Texas	Tenn.
		Range (ppm)	Avg. (ppm)	Avg. (ppm)	Avg. (ppm)
Co		80-325	134	140	22
Cr		70-140	97	55	69
Mo		100-590	320	76	71
Ni		160-890	320	490	89
V		210-680	342	210	200
Ti		3000-10000	7341	1200	1900
Zn		50-1100	300	92	--
U		10-36	20	--	51

TABLE IV

ROCK EVAL PYROLYSIS RESULTS

Sample Number	Tmax (°C)	S_1 (mg/g)	S_2 (mg/g)	S_3 (mg/g)	T.O.C. (wt %)	Hydrogen Index
MAD-8A	429	2.32	49.04	2.16	16.05	305
LIM-3A	422	1.78	47.73	2.82	15.40	311
LIM-3B	422	1.70	40.89	2.46	13.31	308
LIM-4B	421	2.11	50.08	4.83	17.12	296
GIL-10A	422	2.50	56.63	4.51	17.92	316
LIN-1-83-1	422	3.45	67.53	3.15	17.94	376
LIN-1-83-2	422	2.01	44.29	4.89	16.42	270
LIN-1-83-3	423	2.66	59.52	3.52	15.65	380
LIN-1-83-4	423	2.44	57.51	4.67	16.58	346

Tmax	- Temperature index (degrees Celsius)
S_1	- Free hydrocarbons (mg HC/g of rock)
S_2	- Residual hydrocarbon potential (mg HC/g of rock)
S_3	- CO_2 produced from kerogen pyrolysis (mg CO_2/g of rock)
T.O.C.	- Total organic carbon (wt %)
Hydrogen Index	- mg HC/g organic carbon

TABLE V

SATURATE HYDROCARBON ANALYSES: SUMMARY OF PARAFFIN-NAPHTHENE DISTRIBUTION

Sample Number	Paraffin (%)	Isoprenoid (%)	Naphthene (%)
MAD-8A	4.6	0.4	95.0
LIM-3A	6.2	1.0	92.8
LIM-3B	6.2	1.1	92.7
LIN-1-83-1	4.7	0.7	94.6
LIN-1-83-2	5.0	0.8	94.1
LIN-1-83-3	6.1	1.0	93.0
LIN-1-83-4	3.9	0.6	95.5

Whole oil characterization was performed using gas chromatographic/mass spectrometric (GC/MS) techniques. The whole oil analysis by GC/MS is presented in Figure 5. Major compounds and isomers identified in the whole oil samples are listed in Table VII. Compound identification is

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based on the best fit of 31,331 spectra, available standards and evaluation by a mass spectral analyst. The concentration of each compound or isomer is calculated in ppm of the whole oil (weight/weight). Major components of the GC/MS scan are C_{14} (974 ppm), C_{15} (1,048 ppm), C_{16} (1,069 ppm), C_{17} (868 ppm), Dibenzothiophene (1,309 ppm) and Methyldibenzothiophene isomer (836 ppm).

TABLE VI

COMPOSITION OF C_{15+} EXTRACTS

Sample Number	Paraffin-Naphthene (%)	Aromatic (%)	Sulfur (%)	Precipitated Asphaltene (%)	Eluted NSO's (%)	Non-eluted NSO's (%)
MAD-8A	11.0	45.7	4.2	11.7	25.9	1.5
LIM-3A	4.2	13.4	3.5	65.1	7.7	6.1
LIM-3B	3.9	13.3	6.3	65.8	6.9	4.0
LIN-1-83-1	9.1	30.6	2.6	36.6	18.9	2.6
LIN-1-83-2[a]	3.4	10.2	10.9	57.8	13.2	4.8
LIN-1-83-3	10.1	35.4	3.6	26.8	23.2	0.9
LIN-1-83-4	8.4	30.8	10.9	23.2	21.5	5.3

a. Average of two separate sample fraction analyses.

TABLE VII

WHOLE OIL COMPOUND IDENTIFICATION

Scan Number	Compound Identification	(ppm)
832	Tetralin	54
927	n-C_{13}	563
984	Dimethyltetralin isomer	25
1014	n-C_{14}	974
1055	C_2-Alkylnaphthalene isomer	462
1094	n-C_{15}	1048
1170	n-C_{16}	1069
1213	C_2-Alkylbiphenyl isomer	723
1242	n-C_{17}	868
1309	n-C_{18}	482
1314	Dibenzothiophene	1309
1373	n-C_{19}	331
1381	Methyldibenzothiophene isomer	836
1411	2-Methylphenanthrene	243
1458	C_2-Alkyldibenzothiophene isomer	296
1493	C_2-Alkylphenanthrene isomer	189
1611	C_3-Alkylphenanthrene isomer	69
1654	n-C_{24}	67

Non-Destructive Analyses

Non-destructive analytical determinations during this phase of investigation of the Devonian Chattanooga Shale, have included energy dispersive X-ray analyses (EDS) and ^{13}C neutron magnetic resonance analyses (NMR) (1, 3).

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EDS analyses of five different depth intervals of Chattanooga Shale from core hole #8, Madison County, Alabama, were performed on a TN2000 energy dispersive X-ray analysis unit. Eight scans were run for 300 sec each at a tilt angle of 45° and a working distance of 18 mm to 20 mm. Magnification levels varied from 20X to 8,000X.

Major and minor elements indicated by the EDS analyses are Si, Al, K, Ca, Fe, S, Ti and Mg (Table VIII). The elemental identifications show good correlation to previously run X-ray analyses and SEM photomicrograph interpretations of the same shale samples.

TABLE VIII

QUALITATIVE ELEMENT IDENTIFICATION, CHATTANOOGA SHALE, CORE HOLE #8, MADISON COUNTY, ALABAMA

Sample Depth (ft.)	Mineral Identification	Elemental Constituents	
		$K\alpha$ Line	$K\beta$ Line
30.5	quartz	Fe, Si	
31.5	pyrite	Al, Fe, K, S, Si	Fe, K
31.5	clay mineral	Al, Fe, Si	
32.5	pyrite	Al, Fe, K, S, Si	Fe
34.8	clay mineral	Al, Fe, K, Mg, Si, Ti	Fe, K
34.8	clay mineral	Al, Fe, K, S, Si	Fe, K
34.8	clay matrix	Al, Fe, K, S, Si	Fe, K
36.7	clay matrix	Al, Ca, Fe, K, Si, Ti	Ca, Fe, Ti

^{13}C NMR spectra of samples from core hole #9, Madison County, Alabama (Figures 6 and 7), compare favorably to other eastern oil shales in most aspects. However, carbon aromaticity values, fa, are slightly higher (0.53 to 0.58) than most eastern shales (4). Alabama Devonian oil shale contains approximately 0.51 aliphatic carbon, of which 0.25 appears to be convertible to oil (1). This conversion to oil relative to organic carbon content of the shale appears to be in agreement with data given by Miknis and Smith (1982) (5).

SUMMARY

Based on the physical and chemical data obtained to date, the Devonian oil shale rock of north Alabama and south-central Tennessee appears to offer an attractive potential for future resource development. The shale rock appears to have formed in a restrictive marine environment which provided opportunity for the accumulation of marine organic matter to form sufficient kerogen. The shale contains approximately 18% to 22% organic matter which is primarily kerogen. The kerogen has a relatively high H:C ratio indicative of an alginite and/or exinite source (Type 1 and Type II kerogen) and a high proportion of alkane and saturated ring hydrocarbons. However, a few samples have low H:C ratio values and are interpreted to have been formed in a shallow water oxidizing environment. Also, there is a possibility that these low H:C values may represent mixtures of terrestrial and marine organic material suggesting lateral facies changes of the rock from marine to near shore depositional environments. Trace metal values for both the whole rock and the shale oil fraction indicate a generally high V:Ni ratio, also indicative of a marine environment. Other trace metal values are in good agreement with data from other Devonian shales. Throughout the north Alabama and south-central Tennessee study area, the average oil yield from the shale is 13.9 gallon per ton. The highest oil yield values were obtained from the middle and upper parts of the shale sequence. Based on the crude oil composition diagram (11), the Alabama-Tennessee shale oil is classified as an aromatic-intermediate oil. Estimated reserves of inplace shale oil resources in the principal study area, under less than 200 feet of overburden, exceeds 12.5 billion barrels.
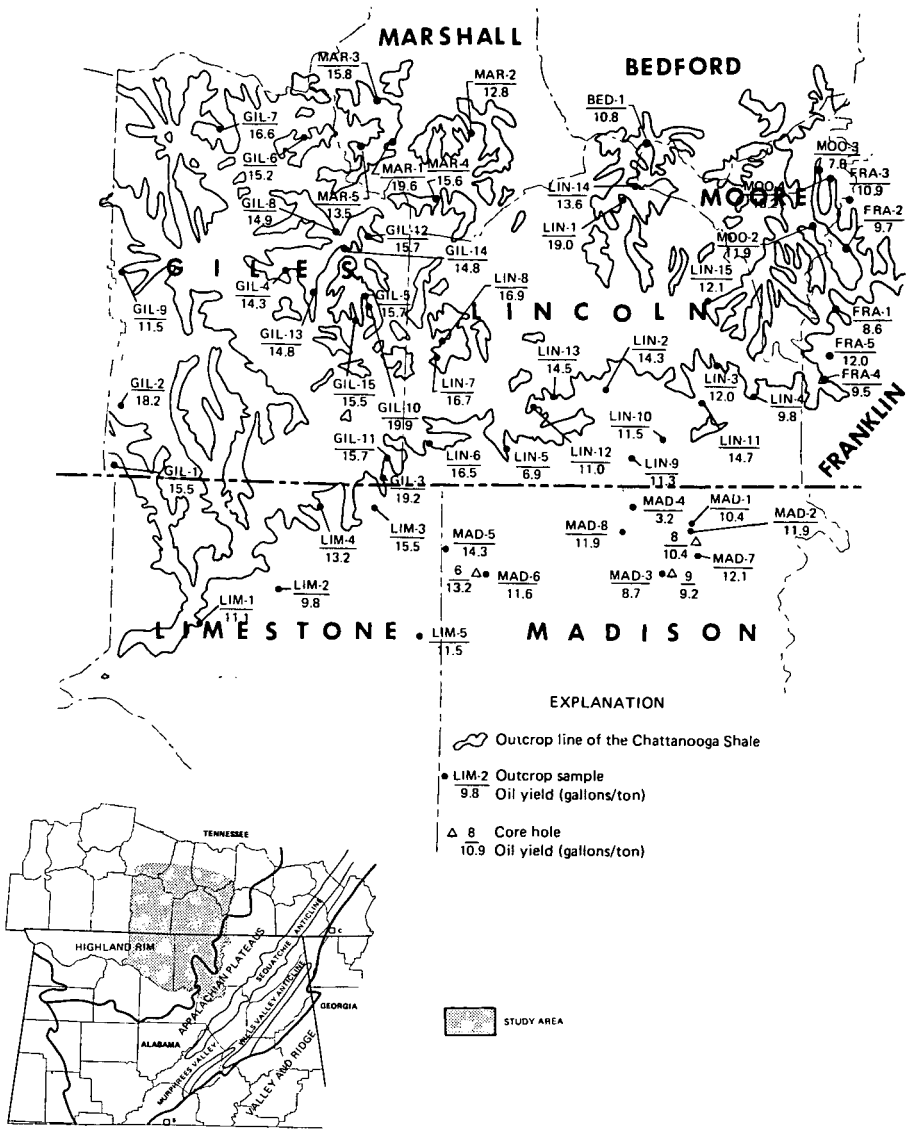
Figure 1.—Study area and general outcrop line of the Chattanooga
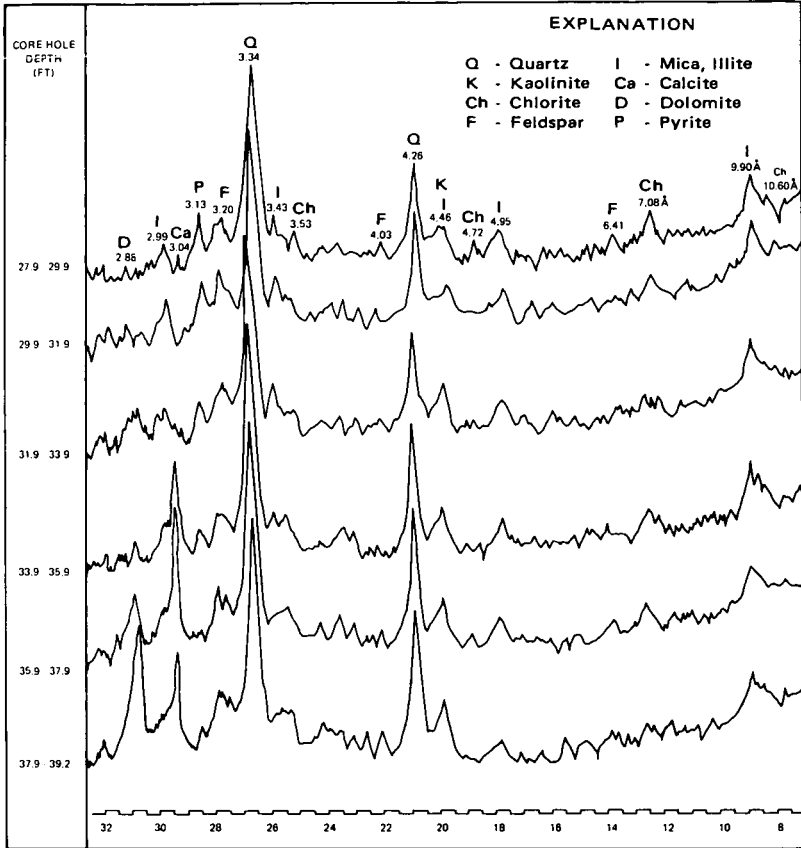Shale, north Alabama and south-central Tennessee.

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Figure 2.—X-ray diffractogram of Chattanooga Shale, core hole
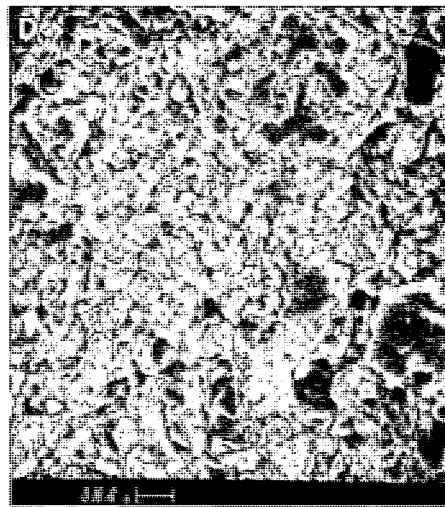#8, Madison County, Alabama.

Figure 3.--Scanning electron photomicrogaphs of selected samples
of Chattanooga Shale, core hole #8, Madison County,
Alabama.

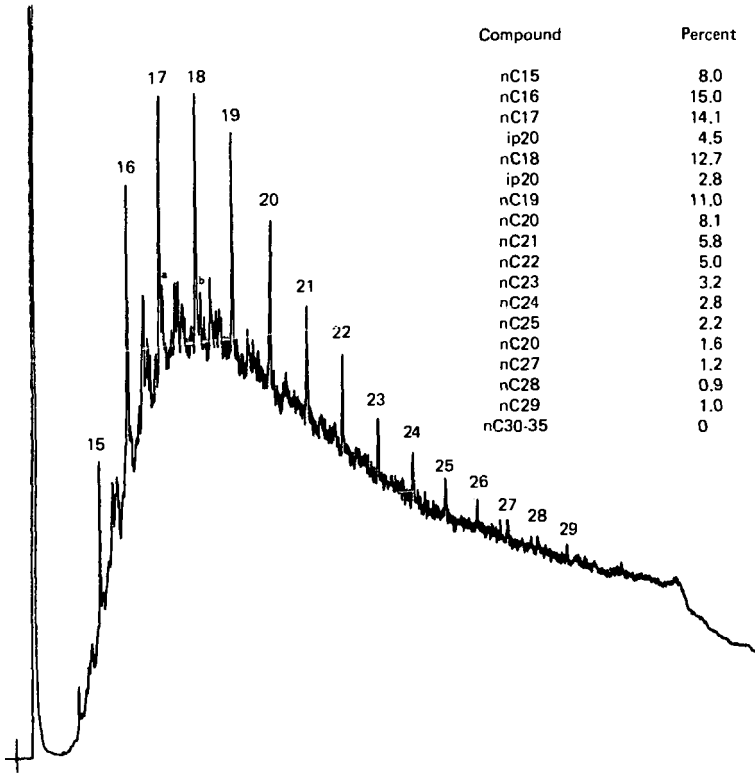| Compound	Percent
nC15	8.0
nC16	15.0
nC17	14.1
ip20	4.5
nC18	12.7
ip20	2.8
nC19	11.0
nC20	8.1
nC21	5.8
nC22	5.0
nC23	3.2
nC24	2.8
nC25	2.2
nC20	1.6
nC27	1.2
nC28	0.9
nC29	1.0
nC30-35	0

Figure 4.--Saturate hydrocarbon analysis-normalized
paraffin distribution.

GC/MS Whole Oil Analysis of Devonian Shale, Alabama

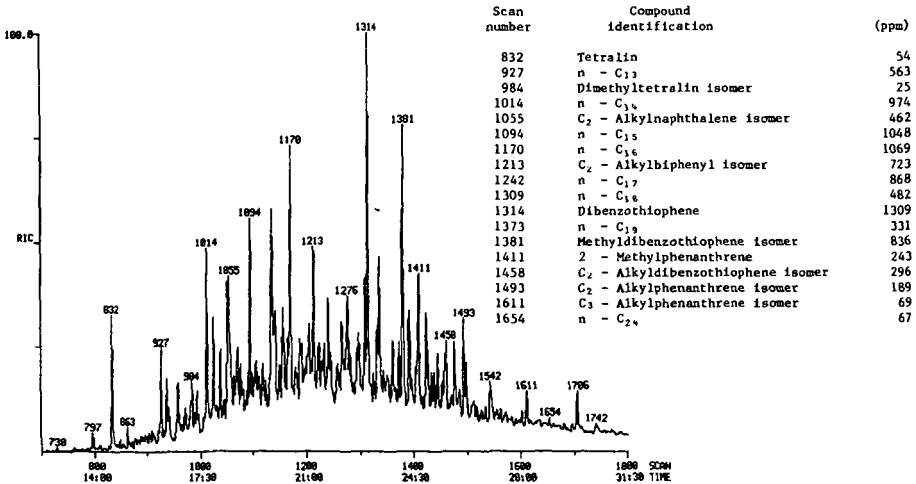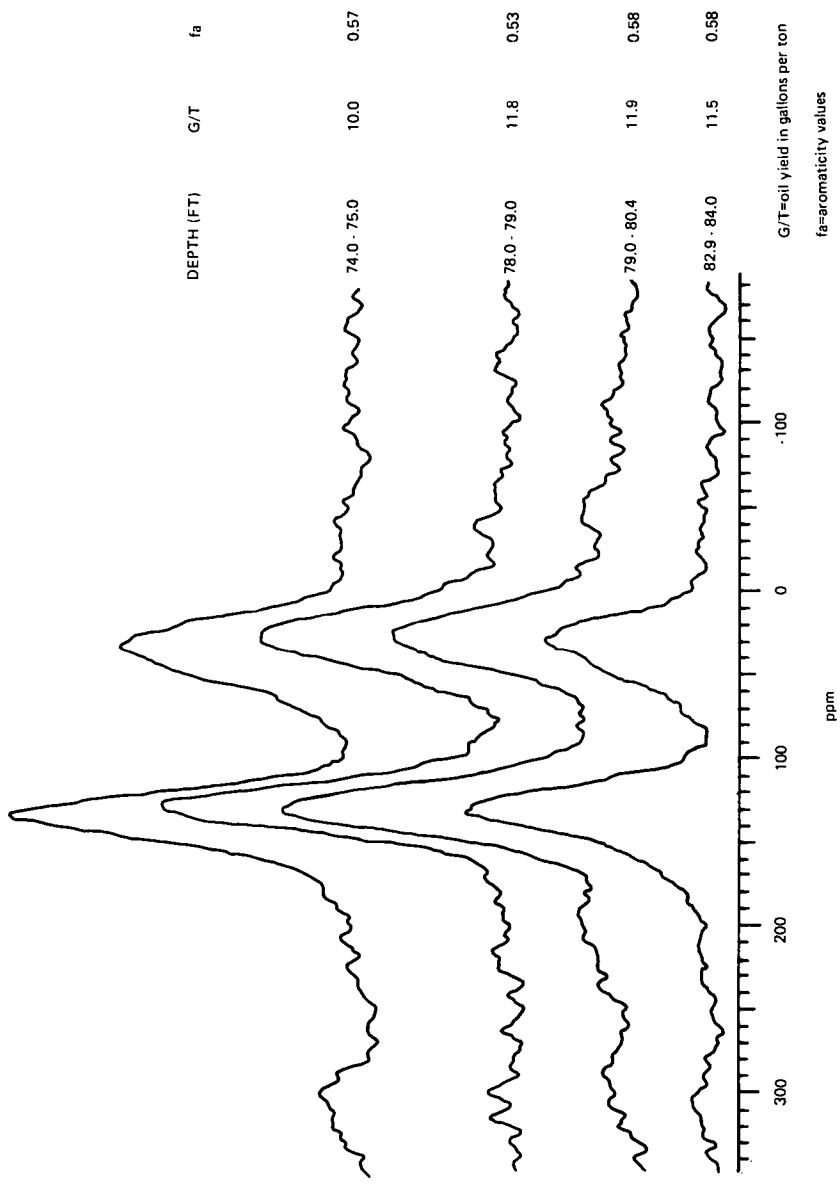| Scan number	Compound identification	(ppm)
832	Tetralin	54
927	$n - C_{13}$	563
984	Dimethyltetralin isomer	25
1014	$n - C_{14}$	974
1055	C_2 - Alkylnaphthalene isomer	462
1094	$n - C_{15}$	1048
1170	$n - C_{16}$	1069
1213	C_2 - Alkylbiphenyl isomer	723
1242	$n - C_{17}$	868
1309	$n - C_{18}$	482
1314	Dibenzothiophene	1309
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1411	2 - Methylphenanthrene	243
1458	C_2 - Alkyldibenzothiophene isomer	296
1493	C_2 - Alkylphenanthrene isomer	189
1611	C_3 - Alkylphenanthrene isomer	69
1654	$n - C_{24}$	67

Figure 5.--GS/MS whole oil analysis of Devonian Shale, Alabama.

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Figure 6.—^{13}C NMR spectra of Chattanooga Shale samples, core hole #9, Madison County, Alabama.
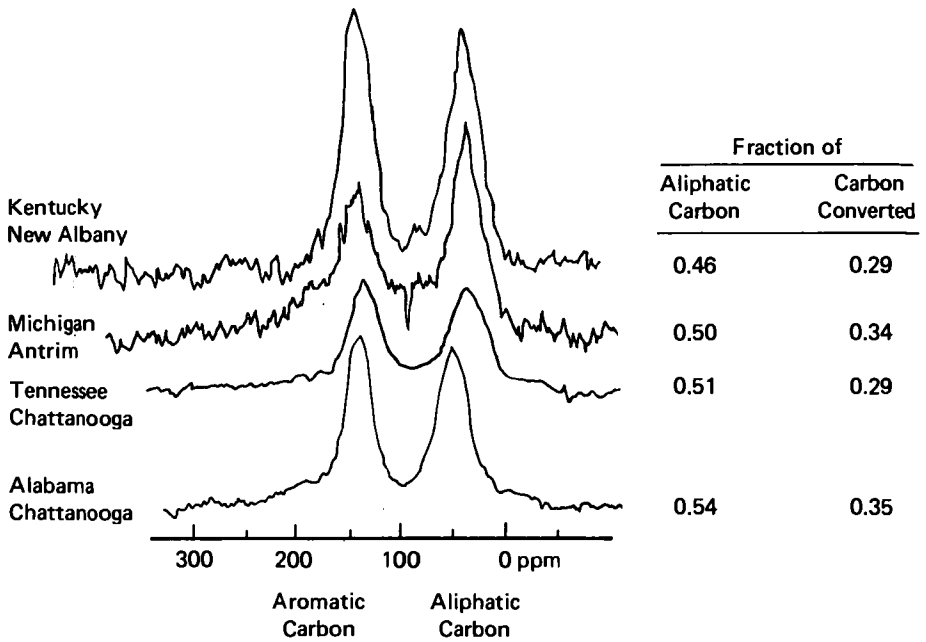
Figure 7.--Comparison of solid state ^{13}C NMR spectra for eastern Devonian Shales (1,5).

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