The Geochemistry of Oils and Gases From the Cumberland Overthrust Sheet in Virginia and Tennessee

By Kristin O. Dennen, Mark Deering, and Robert C. Burruss

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Conversion Factors

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
micrometer (µm)	0.000039	inch (in.)
meter (m)	3.281	foot (ft)
	Volume	
barrel (bbl), (petroleum, 1 barrel=42 gal)	0.1590	cubic meter (m^3)
microliter (µL)	6.102	cubic inch (in^3)
milliliter (mL)	0.06102	cubic inch (in^3)
	Mass	
milligram (mg)	0.00003527	ounce avoirdupois (oz)
	Flow rate	
milliliters per minute (mL/min)	0.06102	cubic inches per minute (cm^3/min)
	Velocity	
centimeters per second (cm/sec)	0.3937	inches per second (in./sec)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

The isotopic composition of carbon (carbon 13, ^{13}C) in methane is reported as the deviation (expressed as $\delta^{13}C$) in units of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard.

The isotopic composition of hydrogen (deuterium, ^{2}H) in methane is reported as the deviation (expressed as $\delta^{2}H$) in per mil relative to the Vienna standard mean ocean water (VSMOW).

The Geochemistry of Oils and Gases From the Cumberland Overthrust Sheet in Virginia and Tennessee

By Kristin O. Dennen,[1] Mark Deering,[2] and Robert C. Burruss[1]

Abstract

This study presents high-resolution gas chromatograms of oils and molecular and isotopic analyses of oil-associated gases from 17 wells producing in the Upper Cambrian to Lower Ordovician Knox Group, the Middle and Upper Ordovician Stones River Group, and the Upper Ordovician Trenton Limestone in the Cumberland overthrust sheet. The wells are located in the Ben Hur and Rose Hill fields in Lee County, Va., and in the Swan Creek field in Hancock and Claiborne Counties, Tenn. They produce oils typical of those from source rocks that are rich in *Gloeocapsomorpha prisca* (*G. prisca*) (Assemblage A-type kerogen). The Rose Hill oils appear to come from a source that contains a higher proportion of Assemblage A-type kerogen than the Ben Hur and Swan Creek oils. Extrapolation of the $\delta^{13}C$ compositions of oil-associated gases to possible kerogen compositions gives estimates of -23 to -24 per mil within the range of isotopic compositions of known *G. prisca* source material. Gases produced from the Knox Group wells in the Swan Creek field are different from those in the Middle and Upper Ordovician reservoirs and come from a source with a broader range of isotopic values. Trends in isotopic and gasoline-range compositional parameters of the oils and associated gas isotopic and molecular compositions are most likely influenced by changes in local source depositional facies.

Introduction

The study area is located in the Cumberland overthrust sheet, which is part of the central Appalachian basin. The Cumberland overthrust sheet is approximately 125 miles (mi) long and 25 mi wide and covers parts of southwestern Virginia, southeastern Kentucky, and northeastern Tennessee (fig. 1). It is bounded on the northwest side by the Pine Mountain thrust fault, on the southeast side by the Clinchport thrust fault, and on the northeast and southwest sides by the Russell Fork and Jacksboro faults, respectively (Miller and Brosge, 1954; Harris and Milici, 1977; Mitra, 1988) (fig. 1). The wells used in this study are located in the Rose Hill and Ben Hur fields in Lee County, Va., and in the Swan Creek field in Hancock and Claiborne Counties, Tenn. (fig. 1).

This area had been explored for oil and gas for almost 100 years, but the first efforts at drilling were unsuccessful because there was little knowledge of the complex regional and local structure (Miller and Brosge, 1954). A producing well was completed in the Trenton Limestone in the Rose Hill field and commercial production started in 1946 (Bartlett, 1989). The Ben Hur field was discovered in 1963 and expanded in 1981 with the drilling of the James Dean No. 1 well (Bartlett, 1989). The first well in the Swan Creek field was completed in 1982 and commercial production began in 1988 (Hatcher and others, 2001). The Ben Hur and Rose Hill fields have produced almost 800,000 barrels of oil (Ryder, 1996; Virginia Center for Coal and Energy Research, 2008). Reserves in the Swan Creek field have been estimated to be over 35 billion cubic feet (bcf) of gas and over 300,000 barrels (42-gallon blue barrels, or bbl) of oil (Hatcher and others, 2001).

Petroleum Geology Overview

Regional Geology

Harris and Milici (1977) divided the Paleozoic in the Cumberland overthrust sheet into three major depositional units: Cambrian through Lower Ordovician, Middle Ordovician through Lower Silurian, and Upper Devonian through Pennsylvanian. Stratigraphic units present in the Rose Hill, Ben Hur, and Swan Creek fields are shown in figure 2. Each unit is separated by a regional unconformity and each sequence records a marine transgression. The units also grade upward from clastic to dominantly carbonate regimes represented by the formation of carbonate banks, lagoons, and shallow-marine-shelf units. Late Proterozoic to early Paleozoic Iapetan rifting was the first of four major Appalachian tectonic episodes recorded in the stratigraphy and structure of

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[1] U.S. Geological Survey, Reston, Va.

[2] Virginia Department of Mines, Minerals and Energy, Division of Gas and Oil, Abingdon, Va.

Figure 1. Map showing the location of the study area. The Cumberland overthrust sheet, bordered on the west by the Pine Mountain thrust fault and on the east by the Clinchport thrust fault, is in the southeastern part of the Appalachian basin on the Tennessee-Virginia-Kentucky border. Colored ovals show the location of oil fields and circles show sample locations. Map is based on Mitra (1988).

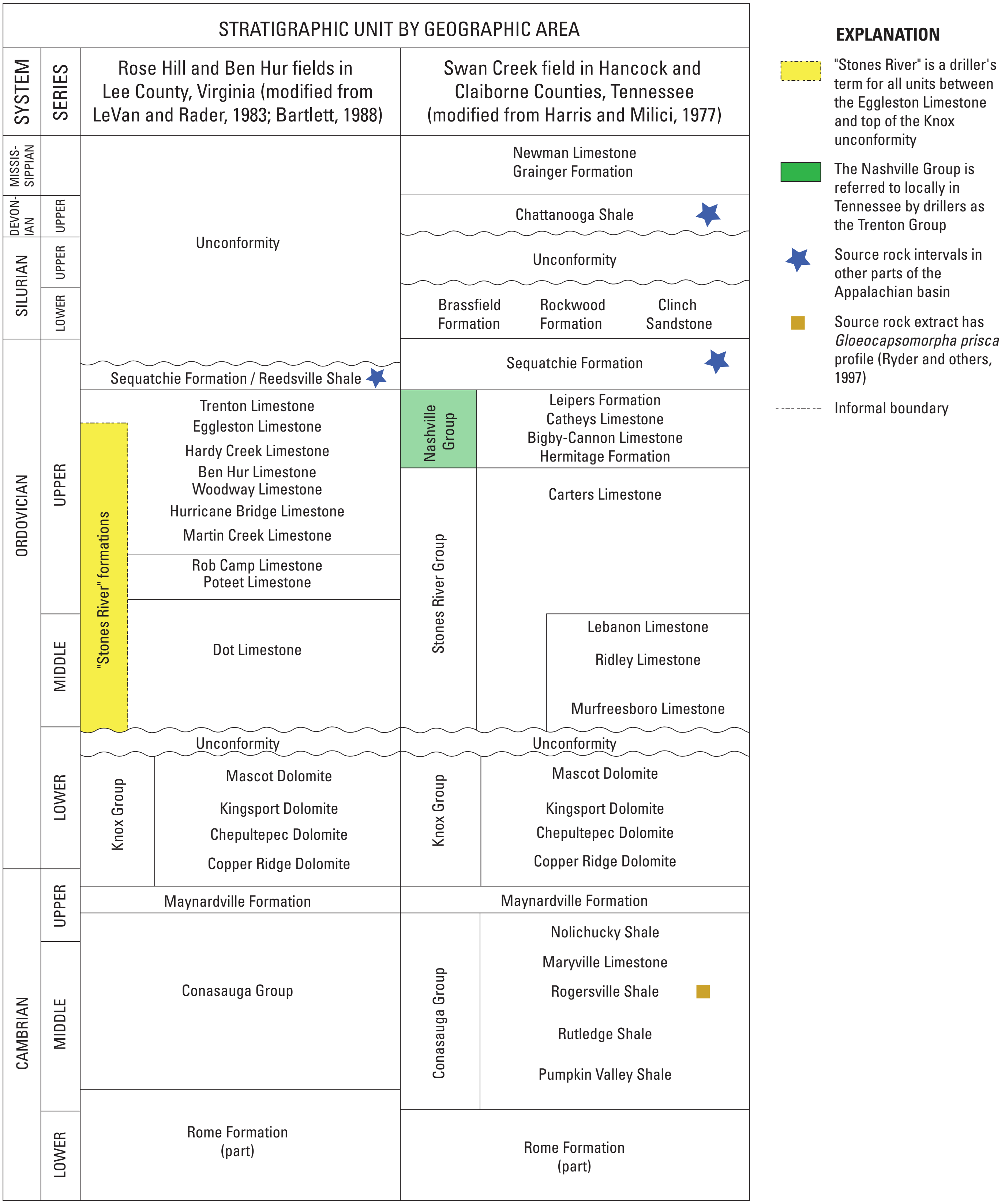


Figure 2. Generalized stratigraphic chart for the Cumberland overthrust sheet showing previous stratigraphic nomenclature for the study area and some current terms used by the oil and gas industry, as used in this report. The chart also shows formations that are source rocks in other parts of the Appalachian basin.

the area. After this, upward-shallowing sequences of the Upper Cambrian and Lower Ordovician Knox Group were deposited on a widespread, stable passive-margin platform where subsidence and depositional rates were generally equal (Pfiel and Read, 1980).

In the Early to Middle Ordovician, the area was uplifted and eroded during a worldwide sea-level drop and a regional transition to an active foreland basin margin, resulting in the post-Knox unconformity (Hatcher and Repetski, 2007). The next three tectonic episodes (the Ordovician Taconian, the Devonian Acadian, and the Carboniferous Alleghanian orogenies) were compressional events. The hydrocarbon sources formed by each of the major depositional units may have generated hydrocarbons from Silurian to Permian time (Milici and others, 2006). In the study area, Middle and Upper Ordovician sediments were deposited on a carbonate ramp between two depositional centers (one to the north and the other to the south, with highlands forming to the east) because of the Taconian orogeny (Read, 1980). The Knox Group carbonates are mainly dolomites, as are parts of the Ordovician carbonate sequences.

Structure of the Cumberland Overthrust Sheet

The complexity of the structure in the Cumberland overthrust sheet is illustrated by the fact that the producing horizon in an oil field can crop out within less than a mile of a well (Bartlett, 1989). The sheet consists of successions of Paleozoic marine strata that have been thrust westward on top of younger units (fig. 3). The Paleozoic sediments reached thermal maturity before folding and faulting; therefore, more thermally mature sequences were thrust on top of less mature strata (Harris and Milici, 1977; Repetski and others, this volume, chap. F.1).

Westward displacement in the Cumberland overthrust sheet ranges from 2 mi on the northeast to more than 13 mi in the southwest with 10 mi of displacement in the Swan Creek area and about 8 mi of displacement in the vicinity of the Rose Hill and Ben Hur fields (Wentworth, 1921; Mitra, 1988). Sequences of Cambrian to Devonian strata are folded and duplicated by a series of imbricate thrust faults that climb along bedding planes in the Cambrian Conasauga Group and Rome Formation up through the Silurian Clinch Formation and Devonian Chattanooga Shale (Harris and Milici, 1977; Mitra, 1988) (fig. 3).

Reservoir Characteristics

Hydrocarbons are trapped in the thrust-faulted anticlines and fault slices above the faults (Ryder, 1996; Hatcher and others, 2001). The Lower Ordovician Mascot Dolomite in the upper part of the Knox Group produces most of the gas in the Swan Creek field and the Middle Ordovician Stones River and Nashville Groups produce most of the oil (table 1). Production in the Swan Creek field currently comes from a fractured anticline between the Clinchport thrust fault (fig. 3) and the Wallen Valley thrust fault where older strata, starting with the Lower Cambrian Rome Formation, overlie a syncline that contains rocks as young as Mississippian (Hatcher and others and others, 2001).

Production from the Ben Hur and Rose Hill wells comes from anticlinal structures in the Bales block, between the Pine Mountain thrust fault (which is exposed on the surface to the west in Kentucky) and the subsurface Bales thrust fault (Nolde, 1992). Most of the hydrocarbon production is from Middle to Upper Ordovician carbonate reservoirs along the axis of the Powell Valley anticline (fig. 3, table 1), with most of the gas production coming from what is called the “Stones River” (a phrase used by drillers in Lee County, Va.), which refers to all the formations between the base of the Trenton Limestone and the unconformity above the Knox Group (see fig. 2); for the purposes of this paper, these formations will be referred to as the “Stones River” formations. Two of the shallowest wells in this study, PO–1 in the Rose Hill field and No. 108 in the Ben Hur field, were drilled in fensters where the Bales block anticlinal structure is exposed by erosion (fig. 3). Recognition and description of these fensters by Butts (1927) and mapping by Miller and Brosge (1954) greatly aided the successful drilling for hydrocarbons in the Ben Hur and Rose Hill fields (Bartlett, 1989).

Reservoirs in the competent nonporous Ordovician limestones and dolomites above the Knox unconformity in the Cumberland overthrust sheet were formed mainly by secondary fracturing during tectonic movements and vug formation during dolomitization (Miller and Brosge, 1954; Nolde, 1992; Ryder, 1996). Fracturing in the Ordovician carbonates is concentrated at the top and bottom of the units (Gathright, 1981). The probability for successful drilling for hydrocarbons in all three fields is enhanced by finding intersecting sets of these fractures (Bartlett, 1989; Hatcher and others, 2001). Below the Knox unconformity, vuggy porosity (resulting from karst formation), subaerial exposure, and migration of deep basin fluids is a major factor in reservoir formation in the Knox Group carbonate reservoirs (Ryder, 1996; Hatcher and others and others, 2001).

Possible Source Rocks

Black shales from either the Ordovician Reedsville Shale (equivalent to the Utica Shale in other parts of the Appalachians) or the Devonian to Mississippian Chattanooga Shale are the most likely sources for the hydrocarbons in the Cumberland overthrust sheet. Middle and Upper Ordovician black shales and argillaceous limestones are source beds in the Appalachian basin from New York to Alabama, with thicknesses ranging from 200 to 400 feet (ft) and total organic carbon (TOC) values ranging from 0.5 to 3 weight percent (Ryder, 1996; Ryder and others, 1998). Ryder and others (1998) concluded that the Middle to Upper Ordovician Utica Shale (Reedsville Shale equivalent; fig. 2) is the hydrocarbon

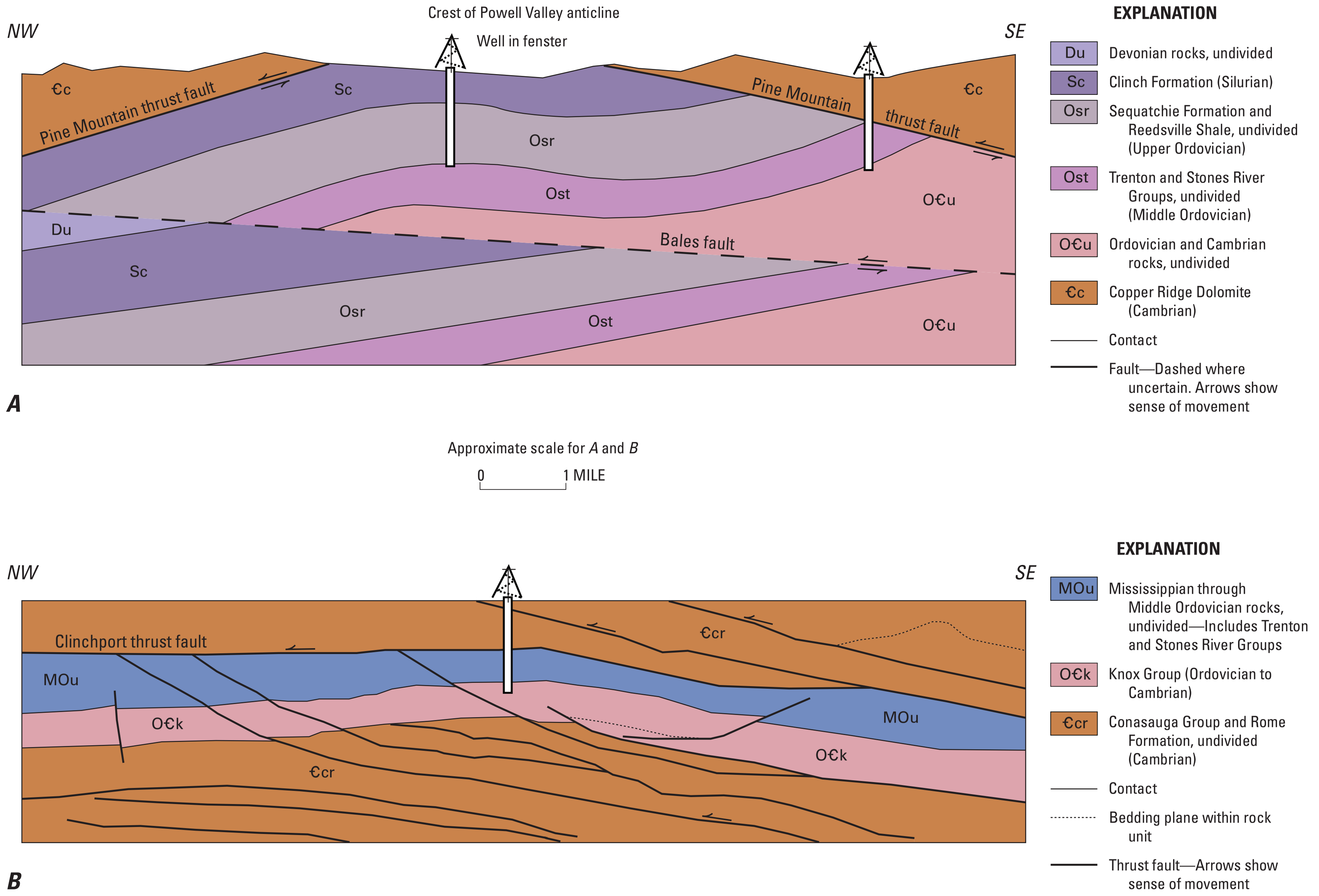


Figure 3. Generalized cross sections of the study area. *A*, Section through the Ben Hur field, Lee County, Va., showing position of a well drilled into a fenster and a well drilled on the southeast flank of the Powell Valley anticline through the Pine Mountain thrust fault. Section is perpendicular to the Powell Valley anticline (see fig. 1). Modified from Bartlett (1989). *B*, Section through the Swan Creek field, Hancock County, Tenn., showing well drilled through the Clinchport thrust fault. Section is perpendicular to the Clinchport thrust fault (see fig. 1). Modified from Hatcher and others (2001).

Table 1. Selected well information.

[Elemental analyses are accurate to within 2 percent. Sulfur and nitrogen values are not reported in this table because they were below the instrumental detection limits in samples from the Ben Hur and Rose Hill oil fields and were not reported for samples from the Swan Creek oil field. Abbreviations are as follows: API, American Petroleum Institute; ft, feet; na, not analyzed; nr, not reported; $\delta^{13}C$, isotopic composition of carbon (carbon 13, ^{13}C) reported as the deviation (expressed as $\delta^{13}C$) in units of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard]

Well name	Type of sample	API number	Oil field	Producing formation(s)	Age of producing formation	Perforated interval (average depth, ft)	Selected analyses for oil samples					
							Carbon (weight percent)	Hydrogen (weight percent)	$\delta^{13}C$ for aromatic fraction (per mil)	$\delta^{13}C$ for saturated fraction (per mil)	API gravity (degrees)	Appendix figure number
No. 108	Oil and gas	4510500438	Ben Hur	Trenton Limestone and "Stones River" formations	Middle Ordovician	1,808	70	12	-27.16	-26.73	45	A1
James Dean No. 1	Oil	4510520452	Ben Hur	Trenton Limestone	Middle Ordovician	2,374	66	11	-27.65	-27.13	46	A2
Yeary No. 1	Oil and gas	4510520719	Ben Hur	Trenton Limestone	Middle Ordovician	2,553	61	11	-27.56	-27.13	43	A3
No. 8709	Oil and gas	4510501123	Ben Hur	Trenton Limestone	Middle Ordovician	3,806	69	12	nr	-26.26	43	A4
No. PO–1	Oil and gas	4510500371	Rose Hill	Clinch Sandstone and Trenton Limestone	Silurian and Ordovician	1,330	79	14	-27.30	-26.98	45	A5
Morgan Hensley No.1	Oil and gas	4510520672	Rose Hill	Trenton Limestone (oil) and "Stones River" formations (gas)	Middle Ordovician	2,711	82	14	-28.61	-28.53	46	A6
No. 8708	Oil and gas	4510501141	Rose Hill	"Stones River" formations	Middle Ordovician	2,910	75	13	-25.21	-22.23	42	A7
No. 1001	Oil and gas	4510505252	Rose Hill	"Stones River" formations	Middle Ordovician	3,083	76	13	-25.36	-22.93	42	A8
No. 1000	Oil and gas	4510504929	Rose Hill	"Stones River" formations	Middle Ordovician	3,096	71	12	-25.84	-25.10	46	A9
Sarah Hensley No. 1	Oil and gas	4510520572	Rose Hill	Knox Group (upper part)	Cambrian and Ordovician	3,994	66	11	-25.74	-24.53	44	A10
Paul Reed No. 5	Gas	4106720018	Swan Creek	Stones River Group	Middle Ordovician	2,155	na	na	nr	nr	nr	No oil sample
Paul Reed No. 2	Oil and gas	4106720013	Swan Creek	Stones River Group	Middle Ordovician	2,958	na	na	-27.45	-27.18	52	A11
Paul Reed No. 4	Gas	4106720017	Swan Creek	Knox Group	Cambrian and Ordovician	4,466	na	na	nr	nr	nr	No oil sample
Paul Reed No. 1	Oil and gas	4106720001	Swan Creek	Knox Group	Cambrian and Ordovician	4,519	na	na	-28.54	-28.82	46	A12
Gary Patton No. 1	Oil and gas	4106720006	Swan Creek	Knox Group	Cambrian and Ordovician	4,740	na	na	-27.13	-26.82	45	A13
Stephen Lawson No. 2	Oil and gas	4106720019	Swan Creek	Nashville Group (oil) and Knox Group (gas)	Cambrian and Ordovician	2,465 (oil) 4,839 (gas)	na	na	-27.53	-27.10	47	A14
Sutton Heirs No. 1	Gas	4106720016	Swan Creek	Knox Group	Cambrian and Ordovician	4,902	na	na	nr	nr	nr	No oil sample
Woodrow Davis No. 1	Gas	4102520136	Swan Creek	Knox Group	Cambrian and Ordovician	4,908	na	na	nr	nr	nr	No oil sample

source not only for Silurian reservoirs in Ohio and Indiana in the United States and Ontario, Canada, but also for the underlying Knox Group, Trenton Group, and Black River Group (Stones River Group equivalent) due to the updip migration of the produced oils. According to Nolde (1992), the Reedsville Shale and the Devonian to Mississippian Chattanooga Shale in Lee County, Va., are still in the zone of oil generation and may be local sources for the Cumberland overthrust sheet reservoirs because they underlie the producing formations in the Bales block (Ryder, 1996).

The *Gloeocapsomorpha Prisca* Enigma

In 1998, U.S. Geological Survey (USGS) analyzed oil samples from four wells in the Swan Creek field in Hancock and Claiborne Counties, Tenn. (U.S. Geological Survey, 1998, unpub. data). The analyses showed evidence that the oils were most likely from an Ordovician carbonate source (Hatcher and others, 2001) because the oil samples had unique characteristics. They had a strong odd-carbon preference in the n-C_9 to n-C_{19} range, with a noticeable reduction in peak height after n-C_{19} (see appendix A). The samples were highly enriched in *n*-alkanes relative to other components and had very low relative concentrations of isoprenoids, including pristane and phytane. The American Petroleum Institute (API) gravity for oil from the Swan Creek field is around 52° (Hatcher and others, 2001).

Martin and others (1963) first noted that this particular profile was unique to early Paleozoic oils. Reed and others (1986), Longman and Palmer (1987), Jacobson and others (1988), and Obermajer and others (2000) are examples of studies where other researchers documented that oils produced from Ordovician carbonate reservoirs in the United States and Canada also had this unique signature. Douglas and others (1991) showed in pyrolysis experiments that the Middle Ordovician Guttenberg oil rock (a driller's term), which is enriched in the remains of the microfossil *Gloeocapsomorpha prisca* (*G. prisca*), produced this profile. The Ordovician Guttenberg Member of the Decorah Formation in Iowa has been well documented as being the purest example in the United States to date of a *G. prisca*-rich oil source rock (Peters and others, 2005). Oil source rocks that are equivalent to the Ordovician Trenton and Stones River Groups in midcontinental and east-central United States also are associated with *G. prisca*-rich source rocks (Reed and others, 1986; Hatch and others, 1987, 1990; Guthrie and Pratt, 1995).

Kerogen is organic material that has a high molecular weight, occurs naturally in sedimentary rocks, and is capable of producing hydrocarbons. Early Paleozoic *G. prisca*-rich kerogens, found in many areas in the world, are similar to those found in Ordovician kukersites of Estonia; the kukersites are mudstones rich in marine carbonates, where *G. prisca* microfossils occur in the organic-rich laminae (Fowler and Douglas, 1984; Reed and others, 1986; Foster and others, 1990; Lille, 2003). *G. prisca*-enriched source rocks, which are primarily Ordovician, formed in marine areas in the tropical range restricted to about 5° on either side of the paleoequator (Tyson, 1995; Peters and others, 2005). These conditions existed during the time at which the Cambrian and Ordovician carbonate formations in the Cumberland overthrust sheet were forming (Pfiel and Read, 1980; Read, 1980).

Although oils with *G. prisca* characteristics are classified as being from an algal source dominated by the lipid-rich membranes of microalgae (Peters and others, 2005), there is no identifiable living organism that produces the polymers that form those microfossils (Blokker and others, 2001). *G. prisca* microfossils appear as nearly structureless clumps and are difficult to identify consistently in thin sections (Jacobson and others, 1988). Oils from *G. prisca*-rich sources have very low relative amounts of isoprenoids, including pristane and phytane, as well as low relative amounts of steranes, terpanes, and other biomarkers (Reed and others, 1986; Longman and Palmer, 1987; Guthrie and Pratt, 1995; Obermajer and others, 1998, 2000). Both characteristics make it very difficult to biologically classify *G. prisca* with certainty. Tyson (1995) and Peters and others (2005) summarized the controversy concerning the biological classification of the *G. prisca* organism and the unique geochemical characteristics reported in oils derived from *G. prisca*-enriched source rocks.

A study by Jacobson and others (1988) of core samples from the mostly carbonate Ordovician Decorah Formation in eastern Iowa, which is similar in age and type to Ordovician carbonate strata of the Appalachian basin, revealed kerogen that occurred as two different morphotypes. One was described as "platy" and designated "Assemblage A"; the other, described as "fluffy," was designated "Assemblage B." Assemblage A microfossils occur in carbonate-dominated environments and produce the characteristic *G. prisca* profile, which is a highly *n*-alkane-rich oil with very low amounts of isoprenoids, such as pristane and phytane. Assemblage B produces oil with more isoprenoids, including pristane and phytane, which is indicative of a marine kerogen deposited in a shale-rich environment.

The *G. prisca* profile in oils is independent of the thermal maturity of the source rock. Reed and others (1986) showed that Ordovician oils with the *G. prisca* profile can come from sources ranging in thermal maturity from 0.65 percent to 1.25 percent calculated vitrinite reflectance (%R_o). *G. prisca*-rich source rocks and their oils exhibit a broad range of isotopic values. The $\delta^{13}C$ value of *G. prisca*-enriched source rocks and oils can vary as much as 9.3 per mil within a single sample (Reed and others, 1986; Hatch and others, 1987; Ludvigson and others, 1996; Mastalerz and others, 2003). ($\delta^{13}C$ represents the isotopic composition of carbon (carbon 13, ^{13}C) in kerogen reported as the deviation in units ($\delta^{13}C$) of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard.)

Recent findings have shown that the *G. prisca* signature in oils can no longer be used to assign the age of the oil source rock to the Ordovician. Evidence of *G. prisca* material has been identified in Late Devonian source rocks in southern Alberta, Canada (Fowler and others, 2004) and in the

Cambrian Rogersville Shale, a local source rock in the Rome trough in West Virginia and eastern Kentucky (Ryder and others, 2005).

To date, there are no reported analyses of any source rocks in the Cumberland overthrust sheet and no *G. prisca*-rich intervals have been reported in well cores from the Ben Hur, Rose Hill, or Swan Creek fields. In order to contribute to the understanding of the nature of the hydrocarbon sources in the Cumberland overthrust sheet, the four oils from the Swan Creek field, initially analyzed in 1998, were re-analyzed in 2006 for this study and complemented with samples collected in 2006 from 13 wells in the nearby Ben Hur and Rose Hill fields (fig. 1). The correlation of source rocks to petroleum accumulations is one of the most critical components of oil and gas assessments based on petroleum systems (Magoon and Dow, 1994). This correlation is the basis for identifying oil migration paths and areas of potential undiscovered resources. Because no analyses of possible source rock candidates in the study area have been reported, analyses of the crude oils and natural gases were used to infer the characteristics of their sources.

Although the results from the biomarker analyses of the Cumberland overthrust sheet oils are included in this study, the interpretations of oil source-rock characteristics in this report are based on compositional ratios calculated from gasoline-range hydrocarbons and isoprenoids. Oil-to-oil and oil-to-source-rock correlations using gasoline-range crude oil compositional ratios are usually complemented by analyses of biomarkers with a higher molecular weight. However, early Paleozoic oils have very low concentrations of biomarkers, making conventional biomarker analyses difficult to interpret (Reed and others, 1986; Guthrie and Pratt, 1995; Peters and others, 2005). For this reason, Obermajer and others (2000) used gasoline-range parameters to refine their biomarker studies of oils in the Williston basin, which included oils from Ordovician source rocks that contained *G. prisca*.

Methods

Oil and gas samples for this study were collected from the Rose Hill and Ben Hur fields in Lee County, southwestern Virginia, in 2006 by the authors. Richard J. Diecchio of George Mason University provided an oil sample from the James Dean No. 1 well. Oil and gas samples from the Swan Creek field in Hancock and Claiborne Counties, Tenn., were collected by Robert D. Hatcher of the University of Tennessee and Christopher Swezey and Robert C. Milici of the USGS in 1998.

Sample Collection

The oil produced in the Ben Hur and Rose Hill fields was pumped from the well head to stock tanks for periodic collection by a tanker truck. The well operator at each well site bailed crude oil samples from the stock tanks in the spring of 2006, with the exception of the sample from well PO–1, which was collected from a well-head drain line. Because the Swan Creek field is primarily a gas field, oil from wells in this field also were stored in well-head tanks before being trucked to the refinery (Hatcher and others, 2001); therefore, we assumed that the Swan Creek oils also were bailed from the stock tanks. In the field, the oil samples were collected in metal cans with screw-on lids. Upon receipt at USGS in Reston, Va., they were split into glass vials, which were capped by screw tops with nonstick liners. Gas samples were collected at the well head in evacuated stainless-steel gas sampling cylinders provided by Isotech Laboratories, Inc., of Champaign, Ill., and were shipped there for analysis.

Instrumental Analysis

Whole Crude Oil

Whole crude-oil samples were analyzed at the USGS Gas Chromatography Laboratory in Reston, Va., using a Hewlett/Packard Model 6890 gas chromatograph (GC) with a 60 meter (m) × 0.32 mm × 0.25 micrometer (µm) DB-1 fused silica capillary column. Samples (0.1 microliter (µL)) were injected manually into a split inlet system (split flow of 15 milliliters per minute (mL/min)) that split the samples 200 to 1. Helium carrier gas carried the samples at a constant velocity of 36 centimeters per second (cm/sec) to a flame ionization detector (FID). After an initial hold at 34°C for 6 min, the programmable oven increased temperature from 34°C to 320°C at 6°C/min and then held the temperature at 320°C for 20 min.

A crude oil sample from Kentucky, which was analyzed under the same conditions and at the same time as the other oil samples, served as a check on instrument performance and reproducibility. Data from the Kentucky oil sample analyses were combined with other analyses of this oil sample conducted over a period of two years in order to determine if the gasoline-range parameter ratios remained constant.

The whole-oil chromatograms were integrated using Justice Innovations, Inc.'s ChromPerfect Spirit version 5.5 software. A baseline chromatogram (injectionless chromatogram), which was run on the same day under the same conditions as the oil samples that were being analyzed, was subtracted from each raw chromatogram. After subtraction of the baseline, the peak areas up to n-C_9 were integrated from the horizontal baseline. After n-C_9, the baseline was reset to integrate peak areas from peak valley to peak valley. Because they are more representative of concentration than peak heights, peak areas were used to calculate compositional ratios shown in the various diagnostic plots.

Elemental, Isotopic, and API Gravity Analysis

Splits of the oil samples were sent to the USGS Organic Geochemistry Laboratory in Denver, Colo., where a Carlo Erba Model 1110 Elemental Analyzer (EA) was used to determine the weight percent of carbon, hydrogen, nitrogen, and sulfur for the oil samples. The oil samples (approximately

2 milligrams) were weighed into tin capsules and introduced to the EA. After undergoing oxygen-enriched combustion, reduction, and oxidation, continuously flowing helium carrier gas transported the gas sample to a gas chromatograph for separation. A thermal conductivity detector then analyzed the gas sample compositions. The Organic Geochemistry Laboratory also analyzed the oil samples for API gravity and for the $\delta^{13}C$ values for the aromatic and saturated fractions.

Standard Biomarker Analysis

The USGS Organic Geochemistry Laboratory in Denver, Colo., also analyzed the oil samples for biomarkers by gas chromatography with a mass-selective detector (GC-MS). The saturated and aromatic hydrocarbon fractions of the crude oil samples were analyzed simultaneously for terpanes, steranes, monoaromatic steroids, and triaromatic steroids by selected ion monitoring of mass-to-charge ratios (*m*/*z*) of 191.1800, 217.1956, 231.1174, and 253.1956, respectively. Quantities were calculated by normalizing the marker peak areas in each sample to the peak area of an internal standard, 5β-cholane, added to each sample. The aromatic fractions of the crude oil samples were analyzed by GC and FID methods described above.

Natural Gas Analysis

Natural gas samples were analyzed for molecular composition by gas chromatography and for stable isotopic composition by isotope-ratio mass spectrometry at Isotech Laboratories, Inc. The carbon and hydrogen isotopic compositions were determined for methane in all samples. Four gas samples from wells in the Ben Hur and Rose Hill fields were submitted for isotopic analysis of $\delta^{13}C$ and $\delta^{2}H$ in propane through pentane, including *iso*-butane. $\delta^{13}C$ represents the isotopic composition of carbon (carbon 13, ^{13}C) in methane reported as the deviation in units ($\delta^{13}C$) of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard. $\delta^{2}H$ represents the isotopic composition of hydrogen (deuterium, ^{2}H) in methane reported as the deviation in units ($\delta^{2}H$) of parts per thousand (per mil) relative to the Vienna standard mean ocean water (VSMOW). The carbon isotopic composition of carbon dioxide was determined for the one sample having a carbon-dioxide concentration above the minimum detection limit for analysis. Natural-gas-geochemistry molecular compositions are based on standards accurate to within 2 percent. Carbon isotope precision is ±0.1 per mil and the precision is ±2 per mil for deuterium.

Results

Oil Geochemistry

The resulting measurements (in weight percent) from the carbon, hydrogen, nitrogen, and sulfur analyses, the $\delta^{13}C$ values for the aromatic and saturated oil fractions, and the API gravity values for the oil samples are shown in table 1. Selected light hydrocarbon compositional ratios are shown in table 2 along with reproducibility data from the in-house oil standard.

Whole-oil gas chromatograms for all the oil samples are shown in appendix A (see appendix A, figures A1 to A14), along with a representative aromatic fraction chromatogram and representative biomarker fragmentograms (appendix B, fig. B1). The profiles of the crude oil samples are presented as integrated peak heights (relative amounts) in millivolts (vertical axis) versus retention time in minutes (horizontal axis). The oil samples showed a strong odd-carbon preference in the n-C_9 to n-C_{19} range, with a noticeable reduction in peak height after n-$C_{19.}$ They were highly enriched in *n*-alkanes relative to other components with a very low relative content of isoprenoids, including pristane and phytane.

Elemental, Isotopic, and API Gravity Analysis

The oil samples from the three fields had high API gravities (43°–52°), with the samples from the Swan Creek field having slightly higher API gravities than samples from the Ben Hur and Rose Hill fields. (Sulfur and nitrogen were below the instrumental detection limit.) Carbon values for the Ben Hur and Rose Hill oil samples ranged from 61.3 to 82.4 weight percent, and hydrogen ranged from 10.6 to 14.1 weight percent. The carbon preference index (CPI) ranged from 1.2 to 1.6. $\delta^{13}C$ values for the aromatic fractions of oil samples from the Ben Hur and Rose Hill fields ranged from -25.2 to -28.5 per mil; for the saturated fractions of the samples, the range was -22.2 to -28.8 per mil.

Biomarker Profiles

Biomarkers for terpanes, steranes, and aromatic compounds were detected in most of the samples although the quantities were generally less than 10 parts per million, which is close to the detection limit for conventional biomarker analyses (appendix B, fig. B1). No steranes or terpanes were reported for the Paul Reed No. 1 well in the Swan Creek field. No triaromatic sterane markers (scanning range of *m*/*z*=231) or monoaromatic sterane markers (scanning range of *m*/*z*=253) were detected in the study oils.

Terpanes

Tricyclic terpanes from C_{19} to C_{29} were present, but the C_{22} tricyclic terpane marker was generally very small relative

Table 2. Selected light hydrocarbon compositional ratios and reproducibility data.

[Compositional ratios (Thompson, 1983) are as follows: A = benzene / *n*-hexane; B = toluene / *n*-heptane; F = *n*-heptane / methylcyclohexane; Heptane value = (*n*-heptane / sum of peak volumes between and including cyclohexane and methylcyclohexane) × 100; *iso*-heptane value = (2-methylcyclohexane + 2,3-dimethylpentane + 3-methylcyclohexanes / 1-*cis*-3-, 1-*trans*-3-, and 1-*trans*-2-dimethylcyclopentane. K^1 (Mango, 1987) = 2-methylhexane + 2,3-dimethylpentane / 3-methylhexane + 2,4-dimethylpentane. Carbon preference index = [(15+17+19) / (14+16+18) + (15+17+19) / (16+18+20)] × 0.5 (numbers refer to number of carbons in *n*-alkanes)]

Well name	Oil-producing formation(s)	Oil field	A	B	F	Heptane value	*iso*-heptane value	K^1	Carbon preference index	Pristane / phytane	Pristane / n-C_{17}	Phytane / n-C_{18}
			Selected light hydrocarbon compositional ratios									
No. 108	Trenton Limestone and "Stones River" formations	Ben Hur	0.07	0.15	2.15	45.26	3.35	1.09	1.51	0.84	0.03	0.09
James Dean No. 1	Trenton Limestone	Ben Hur	0.06	0.13	2.06	42.69	3.64	1.10	1.51	0.91	0.03	0.08
Yeary No. 1	Trenton Limestone	Ben Hur	0.05	0.16	1.86	40.00	3.00	1.08	1.51	0.87	0.03	0.08
No. 8709	Trenton Limestone	Ben Hur	0.10	0.33	1.88	48.63	3.07	1.06	1.47	0.93	0.03	0.10
No. PO–1	Clinch Sandstone and Trenton Limestone	Rose Hill	0.08	0.16	2.20	45.70	2.63	1.08	1.55	0.85	0.03	0.10
Morgan Hensley No. 1	Trenton Limestone	Rose Hill	0.12	0.25	2.48	51.26	2.45	1.08	1.30	1.43	0.12	0.16
No. 8708	"Stones River" formations	Rose Hill	0.19	0.34	2.35	52.61	2.31	1.07	1.62	0.76	0.04	0.17
No. 1001	"Stones River" formations	Rose Hill	0.16	0.28	2.25	55.24	2.07	1.03	1.62	0.78	0.04	0.17
No. 1000	"Stones River" formations	Rose Hill	0.17	0.32	2.49	49.51	2.39	1.10	1.60	0.88	0.04	0.15
Sarah Hensley No. 1	"Stones River" formations	Rose Hill	0.19	0.34	2.41	51.43	2.33	1.08	1.60	0.87	0.04	0.15
Paul Reed No. 2	Stones River Group	Swan Creek	0.05	0.15	1.85	40.30	4.27	1.08	1.40	1.08	0.03	0.06
Paul Reed No. 1	Knox Group	Swan Creek	0.03	0.13	1.04	34.40	4.11	1.09	1.21	1.22	0.05	0.07
Gary Patton No. 1	Knox Group	Swan Creek	0.05	0.13	1.91	44.72	4.36	1.07	1.40	1.05	0.03	0.07
Stephen Lawson No. 2	Nashville Group	Swan Creek	0.02	0.11	1.18	35.27	4.47	1.11	1.45	1.06	0.08	0.18
			Reproducibility of compositional ratios of 14 analyses of a control sample over a period of 2 years									
		Mean standard deviation	0.08	0.31	1.01	24.08	0.85	0.97	1.28	1.86	0.41	0.36
		95 percent confidence interval	0.001	0.002	0.005	0.051	0.001	0.002	0.032	0.060	0.012	0.014

to the other tricyclic terpanes. The C_{19} tricyclic terpane peak was the dominant peak of all of the tricyclics and was often the most abundant of the identified markers. C_{24} tetracyclic terpane was present in similar abundance to the tricyclic terpanes. There was little or no bisnorhopane and no normoretane, except for the oil sample from the Stephen Lawson No. 2 well in the Swan Creek field, which had a measurable normoretane peak.

The C_{27} 18α-trisnorneohopane (Ts)-to-C_{27} 17α-trisnorhopane (Tm) ratio was greater than 1 except for the Gary Patton No. 1 well in the Swan Creek field. The Ts peak was frequently one of the dominant peaks. Neonorhopane was more abundant than norhopane except for the oil sample from the Gary Patton No. 1 well. C30 hopane, although present, was usually not one of the predominant components. The four Swan Creek oil samples had more C_{30} hopane than oil samples from the Rose Hill and Ben Hur wells. The Swan Creek samples had relatively low amounts of the homohopane series, up to C_{33} homohopanes. The Ben Hur and Rose Hill samples had relatively low amounts of homohopanes, ranging from none to C_{35} homohopanes.

Steranes

In all of the oil samples, C_{27} steranes dominated the C_{29} steranes. The Swan Creek samples had more C_{27} 20R ααα steranes than C_{27} 20S βα diasteranes. The Ben Hur and Rose Hill samples had more C_{27} 20S βα diasteranes than C_{27} 20R ααα steranes and they also had more pregnanes.

Aromatic Fraction Biomarkers

Except for the oil sample from the Stephen Lawson No. 1 well in the Swan Creek field, which had only a very small naphthalene peak, 1- and 2-methylnaphthalene were the dominant components in the aromatic fraction of the samples in this study. The oil samples were very low in sulfur-derived biomarkers: there were no measurable dibenzothiophene peaks, phenanthrene was present (but in relatively low amounts), and 9-methylphenanthrene was the dominant methylphenanthrene peak.

Natural Gas Geochemistry

Molecular compositions and isotopic compositions of the natural gas samples are shown in tables 3 and 4, respectively. With the exception of two Swan Creek wells (Sutton Heirs No. 1 and Paul Reed No. 5), all of the wells produced gas as well as oil.

Molecular Composition

Molecular profiles of gas sample compositions are shown in figure 4. None of the gas samples had detectable levels of hydrogen sulfide. Gas samples from two of the wells, No. 8709 and Yeary No. 1, had elevated levels of nitrogen, oxygen, argon, and carbon dioxide and reduced values for the hydrocarbon components, which indicated atmospheric contamination in the samples. These two wells are not shown on figure 4. The trace levels of oxygen were assumed to be the result of low levels of air contamination. The wells producing natural gas from the Ordovician formations in the Rose Hill and Ben Hur fields had approximately half the nitrogen content (1.71 to 2.9 weight percent) compared to the Swan Creek wells from the Knox Group with a range of 4.84 to 5.09 weight percent. Well No. 8708 in the Rose Hill field, which was redrilled down to the top of the upper part of the Knox Group in the spring of 2006, produced gas with little or no hydrogen sulfide (Mark Deering, Virginia Department of Mines, Minerals, and Energy, unpub. data, March, 2006).

Isotopic Composition of Methane, Ethane, Deuterium, and Carbon Dioxide

For all gas samples, the $\delta^{13}C$ values for methane ranged from -44.1 per mil to -50.8 per mil and deuterium values for methane ranged from -164.6 to -215.1 per mil; the gas samples from the Knox Group wells in the Swan Creek field had the least negative values. The Knox Group gas samples from the Swan Creek field were almost identical: the $\delta^{13}C$ values for methane ranged from -44.1 to -44.4 per mil, $\delta^{13}C$ values for ethane ranged from -36.1 to -36.3 per mil, and deuterium values for methane ranged from -164.6 to -169.6 per mil. For the four deeper wells in Lee County, the $\delta^{13}C$ values for methane in the Rose Hill field were -47.4 per mil and -47.6 per mil and the $\delta^{13}C$ values for methane in the Ben Hur field were -45.1 per mil and -45.5 per mil. The shallowest wells (in the fensters) had the most negative $\delta^{13}C$ values for methane: -49.4 per mil in the Ben Hur field and -50.8 per mil in the Rose Hill field.

Only the No. 1001 well, producing from the “Stones River” formations in the Rose Hill field, had enough carbon dioxide for $\delta^{13}C$ analysis. The $\delta^{13}C$ composition of carbon dioxide from this well was -6.2 per mil.

Isotopic Composition of Gases With Higher Carbon Numbers

Of the four samples submitted for isotopic analyses of gases with a higher carbon number (table 4), two of the samples were from wells located in the fenster: (1) No. 108 in the Ben Hur field, producing from the Trenton Limestone and “Stones River” formations, and (2) PO–1 in the Rose Hill field, producing from the Clinch Formation and Trenton Limestone. The other two samples were from the No. 8708 and the No. 1001 wells located in the Rose Hill field, producing from the “Stones River” formations. Gases with higher carbon numbers from the Swan Creek field were not analyzed for isotopic composition.

The $\delta^{13}C$ values for ethane from the wells located in the fenster (-33.6 and -34.0 per mil) were more negative than

Table 3. Molecular composition of gases.

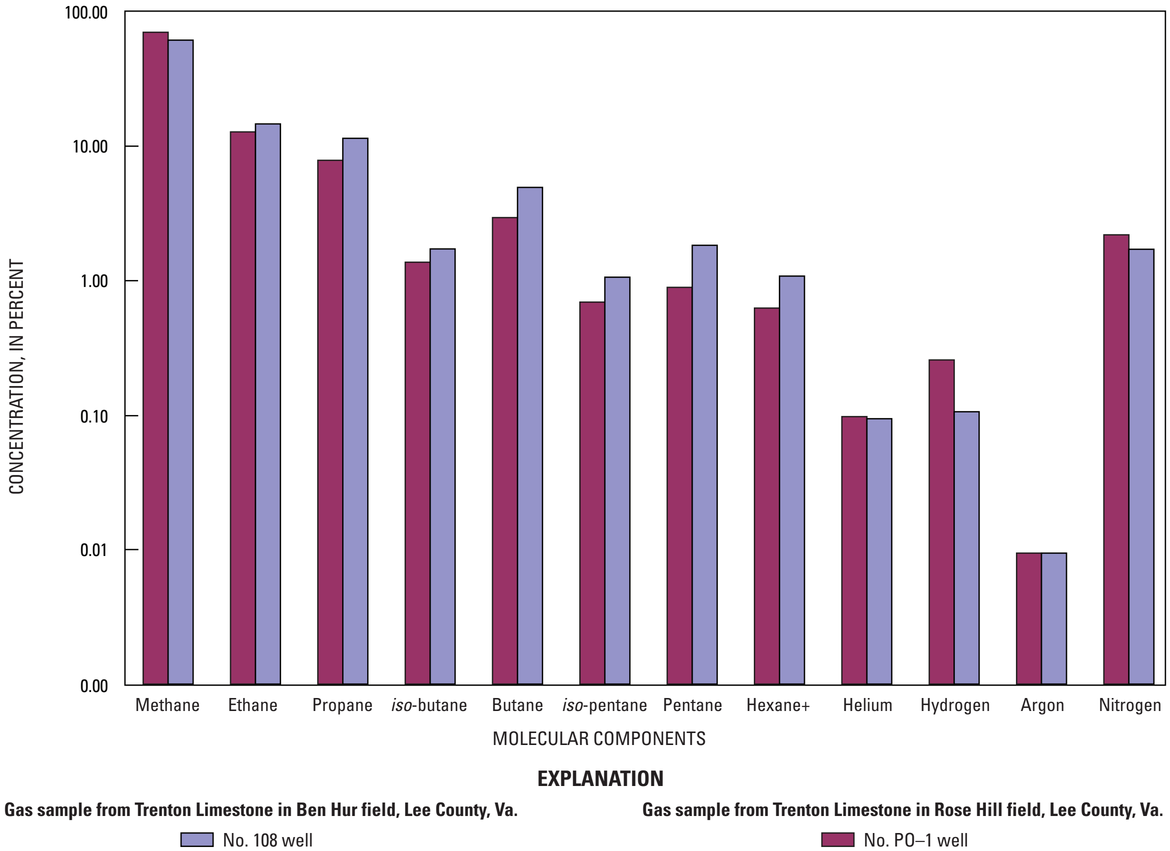
[Chemical analyses are based on standards accurate to within 2 percent. Hydrogen sulfide gas was not detected in any of the gas samples. na, not analyzed]

Well name	Oil field	Producing formation(s)	Average depth of perforated interval (ft)	Molecular composition of gases, in percent													
				Helium	Hydrogen	Argon	Oxygen	Carbon dioxide	Nitrogen	Methane	Ethane	Propane	*iso*-butane	*n*-butane	*iso*-pentane	*n*-pentane	Hexane+
No. 108	Ben Hur	Trenton Limestone and "Stones River" formations	1,808	0.10	0.26	0.01	0.04	0.04	2.19	70.23	12.77	7.84	1.37	2.94	0.69	0.89	0.63
Yeary No. 1	Ben Hur	Trenton Limestone	2,553	0.03	0.03	0.28	6.13	0.12	23.83	46.77	8.72	6.26	1.50	3.15	1.04	1.27	0.87
No. 8709	Ben Hur	Trenton Limestone	3,806	0.01	0.01	0.65	13.96	0.09	52.00	25.98	4.11	1.81	0.27	0.57	0.12	0.17	0.27
No. PO–1	Rose Hill	Clinch Sandstone and Trenton Limestone	1,330	0.09	0.11	0.01	0.05	0.03	1.71	61.34	14.61	11.43	1.72	4.93	1.06	1.83	1.08
Morgan Hensley No. 1	Rose Hill	"Stones River" formations	2,711	0.09	0.03	0.02	0.01	0.02	2.15	80.16	9.90	4.86	0.75	1.19	0.27	0.31	0.25
No. 8708	Rose Hill	"Stones River" formations	2,910	0.11	0.03	0.02	0.02	0.01	2.44	84.45	7.90	3.23	0.45	0.76	0.16	0.20	0.21
No. 1001	Rose Hill	"Stones River" formations	3,083	0.12	0.04	0.02	0.01	0.18	2.90	83.45	7.76	3.19	0.48	0.87	0.23	0.35	0.41
No. 1000	Rose Hill	"Stones River" formations	3,096	0.08	0.03	0.01	0.01	0.03	2.01	81.20	9.14	4.64	0.77	1.25	0.29	0.32	0.22
Sarah Hensley No. 1	Rose Hill	Knox Group (upper part)	3,994	0.10	0.03	0.02	0.06	0.01	2.54	83.38	8.33	3.60	0.53	0.83	0.18	0.20	0.18
Paul Reed No. 5	Swan Creek	Stones River Group	2,155	0.16	0.13	0.02	0.03	0.03	2.89	85.19	6.14	2.70	0.42	0.93	0.27	0.35	0.75
Paul Reed No. 2	Swan Creek	Stones River Group	2,958	0.08	0.04	0.02	0.01	0.02	2.33	70.89	10.49	8.30	1.56	3.41	0.87	0.97	1.02
Paul Reed No. 4	Swan Creek	Knox Group	4,466	0.12	0.06	0.04	na	na	4.90	89.37	3.52	0.91	0.21	0.32	0.13	0.13	0.30
Paul Reed No. 1	Swan Creek	Knox Group	4,519	0.12	0.09	0.04	na	na	4.84	89.03	3.61	0.97	0.23	0.35	0.15	0.15	0.42
Gary Patton No. 1	Swan Creek	Knox Group	4,740	0.12	0.05	0.04	na	na	4.86	89.36	3.53	0.92	0.22	0.32	0.13	0.13	0.33
Stephen Lawson No. 2	Swan Creek	Knox Group	4,839	0.12	0.03	0.03	na	na	4.82	89.31	3.54	0.93	0.22	0.33	0.14	0.13	0.40
Sutton Heirs No. 1	Swan Creek	Knox Group	4,902	0.12	0.08	0.04	na	na	4.92	89.11	3.49	0.96	0.23	0.35	0.15	0.15	0.41
Woodrow Davis No. 1	Swan Creek	Knox Group	4,908	0.13	0.08	0.04	0.01	0.13	5.09	88.66	3.65	1.06	0.25	0.38	0.14	0.14	0.25

Table 4. Isotopic composition of carbon and hydrogen in gas samples.

[Isotopic composition of carbon (carbon 13, ^{13}C) is reported as the deviation (expressed as δ^{13}C) in units of parts per thousand (per mil) relative to the Vienna Peedee belemnite (VPDB) standard. Isotopic composition of hydrogen (deuterium, ^{2}H) is reported as the deviation (expressed as δ^{2}H) in units of parts per thousand (per mil) relative to the Vienna standard mean ocean water (VSMOW). Isotope precision is ±0.1 per mil for carbon 13 and ±2 per mil for deuterium. Abbreviations are as follows: ft, feet; na, not analyzed]

Well name	Oil field	Perforated interval (average depth, ft)	Isotopic composition (per mil)												
			δ^{13}C carbon dioxide	δ^{13}C methane	δ^{2}H methane	δ^{13}C ethane	δ^{2}H ethane	δ^{13}C propane	δ^{2}H propane	δ^{13}C *iso*-butane	δ^{2}H *iso*-butane	δ^{13}C *n*-butane	δ^{2}H *n*-butane	δ^{13}C *n*-pentane	δ^{2}H *n*-pentane
No. 108	Ben Hur	1,808	na	-49.4	-208.3	-33.6	-148.8	-29.0	-125.7	-29.3	-112.2	-27.1	-116.2	-26.1	-110.9
Yeary No. 1	Ben Hur	2,553	na	-45.1	-181.2	na	na	na	na	na	na	na	na	na	na
No. 8709	Ben Hur	3,806	na	-45.5	-182.1	na	na	na	na	na	na	na	na	na	na
No. PO–1	Rose Hill	1,330	na	-50.8	-215.1	-34.0	-155.0	-29.6	-128.3	-30.2	-113.7	-27.9	-123.8	-26.5	-116.0
Morgan Hensley No. 1	Rose Hill	2,711	na	-47.4	-179.2	na	na	na	na	na	na	na	na	na	na
No. 8708	Rose Hill	2,910	na	-47.5	-178.3	-31.6	-122.6	-29.0	-117.2	-30.9	-108.5	-27.1	-114.0	-24.8	-109.9
No. 1001	Rose Hill	3,083	-6.2	-47.6	-183.9	-31.9	-134.9	-29.1	-130.3	-31.0	-114.2	-27.1	-121.9	-25.1	-118.9
No. 1000	Rose Hill	3,096	na	-47.4	-183.5	na	na	na	na	na	na	na	na	na	na
Sarah Hensley No. 1	Rose Hill	3,994	na	-47.6	-181.8	na	na	na	na	na	na	na	na	na	na
Paul Reed No. 5	Swan Creek	2,155	na	-46.0	-182.2	-33.5	na	-29.0	na	na	na	-27.3	na	na	na
Paul Reed No. 2	Swan Creek	2,958	na	-45.0	-174.6	-33.5	na	-29.0	na	na	na	-27.2	na	na	na
Paul Reed No. 4	Swan Creek	4,466	na	-44.1	-169.4	-36.3	na	-28.8	na	na	na	-26.3	na	na	na
Paul Reed No. 1	Swan Creek	4,519	na	-44.2	-169.4	-36.2	na	-28.7	na	na	na	-26.3	na	na	na
Gary Patton No. 1	Swan Creek	4,740	na	-44.3	-169.6	-36.2	na	-28.7	na	na	na	-26.3	na	na	na
Stephen Lawson No. 2	Swan Creek	4,839	na	-44.4	-169.3	-36.3	na	-28.8	na	na	na	-26.3	na	na	na
Sutton Heirs No. 1	Swan Creek	4,902	na	-44.2	-164.6	-36.2	na	-28.7	na	na	na	-26.3	na	na	na
Woodrow Davis No. 1	Swan Creek	4,908	na	-44.4	-166.7	-36.1	na	-28.6	na	na	na	-26.4	na	na	na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CONCENTRATION, IN PERCENT
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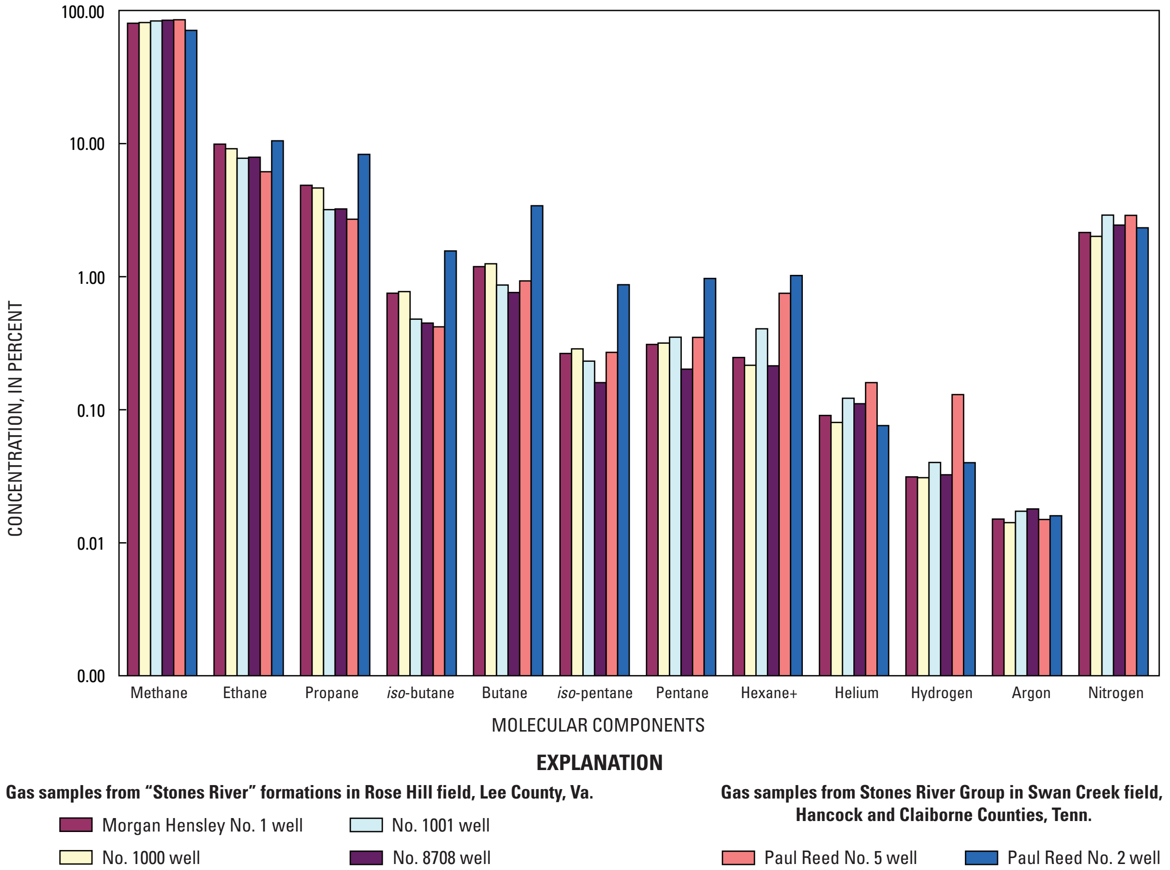
Ethane
Propane
iso-butane
Butane
iso-pentane
Pentane
Hexane+
Helium
Hydrogen
Argon
Nitrogen
MOLECULAR COMPONENTS
EXPLANATION
Gas sample from Trenton Limestone in Ben Hur field, Lee County, Va.
No. 108 well
Gas sample from Trenton Limestone in Rose Hill field, Lee County, Va.
No. PO–1 well

A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CONCENTRATION, IN PERCENT
Methane
Ethane
Propane
iso-butane
Butane
iso-pentane
Pentane
Hexane+
Helium
Hydrogen
Argon
Nitrogen
MOLECULAR COMPONENTS
EXPLANATION
Gas samples from "Stones River" formations in Rose Hill field, Lee County, Va.
Morgan Hensley No. 1 well
No. 1001 well
No. 1000 well
No. 8708 well
Gas samples from Stones River Group in Swan Creek field, Hancock and Claiborne Counties, Tenn.
Paul Reed No. 5 well
Paul Reed No. 2 well

B

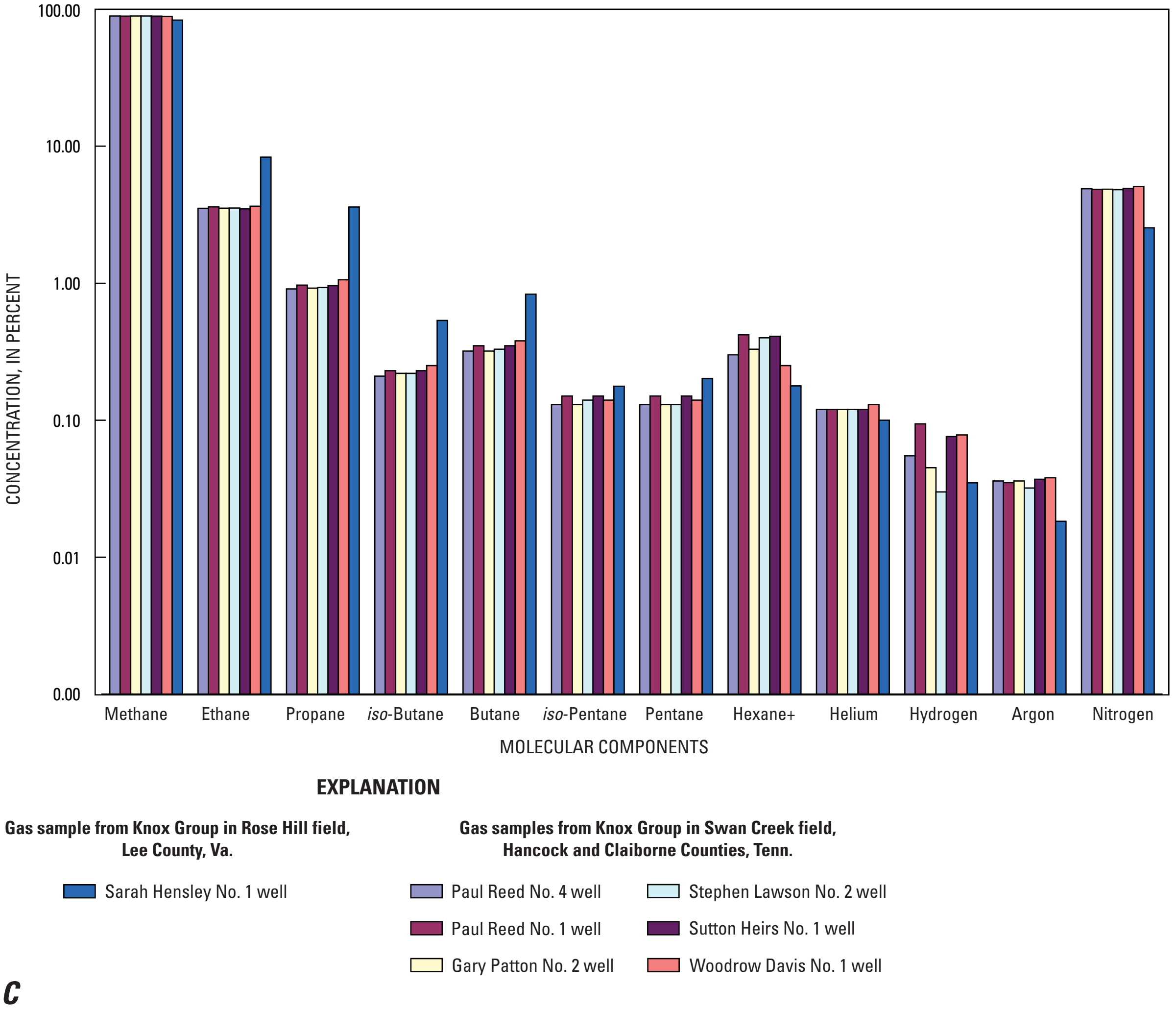


Figure 4 (facing page and this page). Bar charts showing percentage of each molecular component in the analyzed gas samples from the Cumberland overthrust sheet. *A*, Gas samples from the Trenton Limestone in Virginia and the Nashville Group in Tennessee. *B*, Gas samples from the "Stones River" formations in Virginia and the Stones River Group in Tennessee. *C*, Gas samples from the Knox Group.

those from the deeper wells in the Rose Hill field (-31.6 and -31.9 per mil). This was also true for the $\delta^{2}H$ values for ethane from the fenster wells (-148.8 and -155.0 per mil) compared with those from the deeper wells (-122.6 and -134.9 per mil). The range of $\delta^{13}C$ values for propane was from -29.0 to -29.6 per mil, with the most negative value coming from one of the wells located in the fenster. The $\delta^{2}H$ values for propane (-117.2 and -130.3 per mil) in the deeper Rose Hill wells were at the extreme ends of the range of values; the wells located in the fenster in the Rose Hill field had $\delta^{2}H$ values for propane of -125.7 and -128.3 per mil.

For all four gas samples, the $\delta^{13}C$ values for *iso*-butane ranged from -29.3 to -31.0 per mil and the $\delta^{2}H$ values for *iso*-butane ranged from -108.5 to -114.2 per mil; the deeper Rose Hill wells had both the most negative and the most positive $\delta^{2}H$ values. Gas samples from three of the wells had $\delta^{13}C$ values for *n*-butane of -27.1 per mil. The PO–1 well, which is located in the fenster in the Rose Hill field, had the most negative $\delta^{13}C$ *n*-butane value of -27.9 per mil. The $\delta^{2}H$ values for *n*-butane ranged from -114.0 to -123.8 per mil, with the most negative value coming from the PO–1 well. The $\delta^{13}C$ values for pentane from the wells in the fenster (-26.1 and -26.5 per mil) were more negative than those in the deeper wells in the Rose Hill field (-24.8 and -25.1 per mil). The $\delta^{2}H$ values for pentane in the four wells ranged from -109.9 to -118.9 per mil, with the deeper Rose Hill wells having the most extreme values.

Discussion

Data Quality

The total quantity of gasoline-range hydrocarbons can be affected by evaporative loss, which may be seen in relative amounts in the gas chromatographic signatures of the oil samples in this study. For example, the profile for the Yeary No. 1 well (appendix A, fig. A3) exhibited higher peak heights in the n-C_5 to n-C_7 range than in the n-C_{8+} range. This sample (and others with this type of profile) presumably represented relatively fresh samples because it had a greater abundance of the light hydrocarbons relative to the *n*-alkanes with higher carbon numbers and a flat baseline. The sample from the No. 8709 well (appendix A, fig. A4) exhibited reduced peak heights in the lighter *n*-alkane range compared to the sample from the Yeary No. 1 well, which indicates a relatively greater loss of light hydrocarbons in the sample from the No. 8709 well. This evaporative loss could have been caused by sample handling and storage.

According to Thompson (1983), Ten Haven (1996), Mango (1997), Jarvie (2001), and references therein, compositional ratios in oil samples are very useful for assessing oil type, maturation, and other characteristics because the C_4-to-C_8 hydrocarbon ratios remain relatively constant. C_4 to C_8 hydrocarbons have similar boiling points and evaporative loss should not affect relative abundance. Over a period of two years, the gasoline-range parameters collected for the Kentucky in-house standard oil sample (stored at room temperature in a capped glass vial) remained relatively constant with standard deviations ranging from 0.001 to 0.06 and 95 percent confidence intervals ranging from 0.0001 to 0.022 (table 2). Ten Haven (1996) found that ratios can remain constant even after oil samples are stored for 20 years at room temperature.

Aerobic biodegradation can also affect data collected from oil samples by selectively removing *n*-alkanes, such as propane, and contributing compounds that cannot be identified using routine gas chromatography (Connan, 1984; Wenger and others, 2002). The Morgan Hensley No. 1 well profile (appendix A, fig. A6) exhibited an easily measurable pristane and phytane peak, a more extreme reduction in peak heights of the lighter *n*-alkanes, and an unresolved complex mixture “hump,” which did not appear in chromatograms for the other oil samples. The loss of lighter *n*-alkanes in the Morgan Hensley No. 1 well sample most likely was due to both evaporative loss and slight aerobic biodegradation (using the criteria of Wenger and others, 2002) because the oil from which this sample was taken had been stored in the holding tank for over a year, according to the well operator.

Isoprenoids in oil samples from Ordovician source rocks varied in abundance from almost undetectable to that typical of most oils generated from Phanerozoic marine sediments (Jacobson and others, 1988). The small amounts of the isoprenoids pristane and phytane in the oil samples in this study were confirmed using a gas chromatograph with a mass selective detector.

Compositional Trends in Oil From the Cumberland Overthrust Sheet

Gas Chromatographic and Biomarker Profiles

The oil samples exhibited gas chromatographic profiles similar to oils associated with *G. prisca*-rich sources from Trenton Group and Stones River Group equivalent sources in the midcontinental and east-central United States (Reed and others, 1986; Hatch and others, 1987, 1990; Guthrie and Pratt, 1995). Biomarkers in the oil samples in this study (appendix B, fig. B1) also were similar to those reported in oils from *G. prisca*-rich Ordovician source rocks in basins in the midcontinental United States and in Canada (Longman and Palmer, 1987; Obermajer and others, 1998, 2000). The abundance of biomarkers generally was very low, tricyclic terpanes dominated the terpane profile, there were more diasteranes than steranes, and the C_{30} homohopanes were relatively scarce. Normoretane, bisnorhopane, and moretane were rare or not reported. The oil samples in this study appeared to have less C_{30} hopane and C_{30} homohopanes than was reported for Ordovician oils from reservoirs in rocks equivalent to the Trenton and Stones River Groups in Canada and the midcontinental United States (Longman and Palmer, 1987; Obermajer and others, 1998, 2000). The very low amounts of organic sulfur compounds in the oil samples in this study were consistent with observations of Ordovician oils by Douglas and others (1991) and Hughes and others (1995).

Light Hydrocarbon Parameters

Oils from *G. prisca*-rich source rocks are typically low in branched and cyclic compounds and have a predominance of *n*-alkanes compared with oils from younger Paleozoic sources. This relation is shown in figure 5, where *n*-alkane enrichment in oils is shown by the *n*-heptane-to-methylcyclohexane ratio (paraffinicity) and enrichment in branched and cyclic compounds is shown by the toluene-to-*n*-heptane ratio (aromaticity) (Thompson, 1983). The most extreme examples of *n*-alkane enrichment with low amounts of aromatic compounds are from oils from the Ordovician Red River Formation of the Williston basin. The sources for the Red River oils are known to be the *G. prisca*-rich kukersites in the Upper Ordovician Bighorn Group (Osadetz and others, 1992; Osadetz and Snowdon, 1995). Of all the oil samples in this study, the samples from the Rose Hill field were the closest in composition to the Red River oils in *n*-alkane enrichment, but they were slightly more aromatic. The samples from the Ben Hur and Swan Creek fields trend in composition toward the Devonian and Mississippian oils (Thompson, 1983).

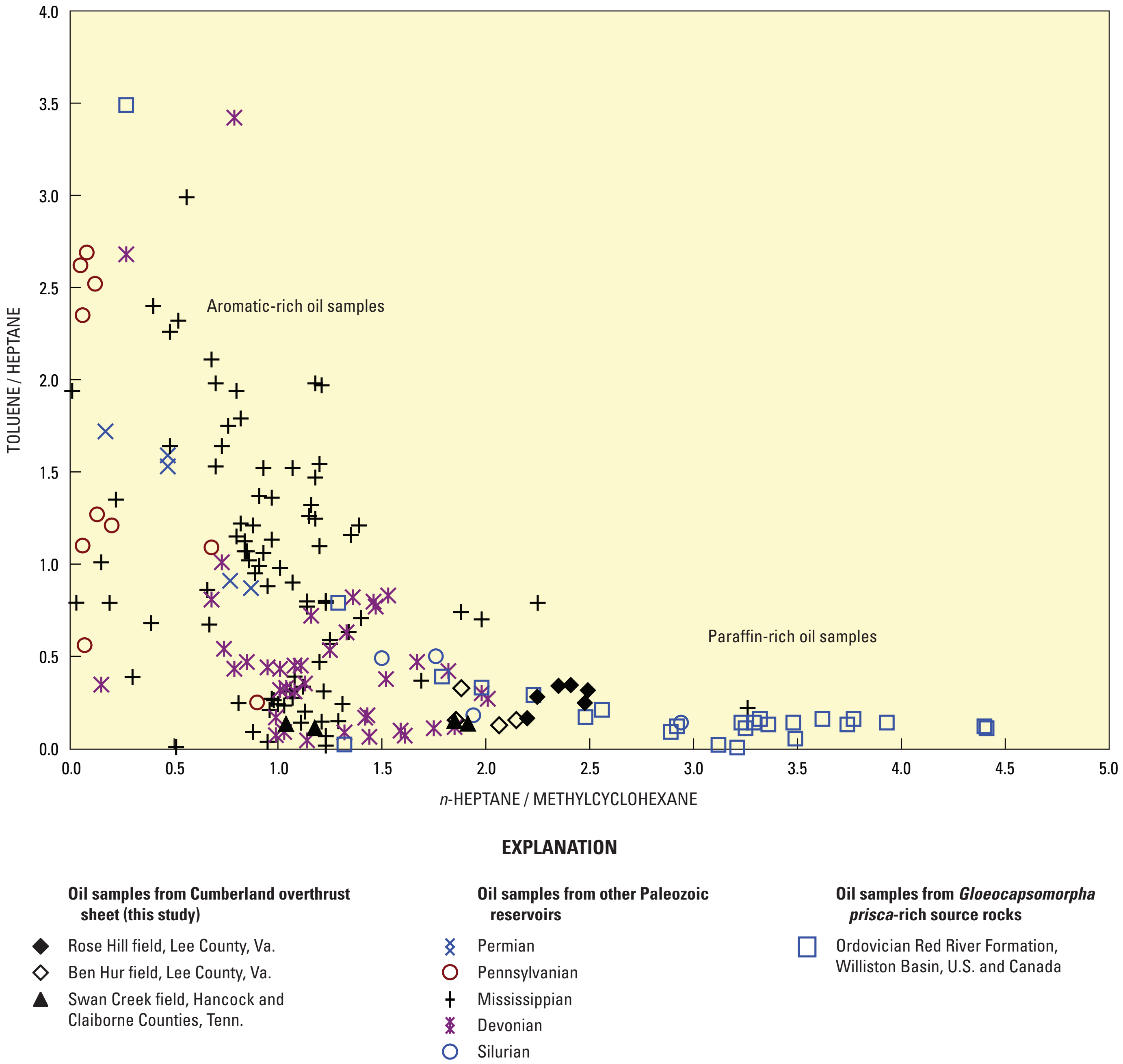


Figure 5. Graph showing the *n*-heptane-to-methylcyclohexane ratio versus the toluene-to-*n*-heptane ratio of oil samples from the Cumberland overthrust sheet and (for comparison) from oil samples from other Paleozoic reservoirs in the United States and Canada (Thompson, 1983). Data for other Paleozoic reservoirs is from Thompson (1983), Osadetz and others (1992), and Jarvie (2001).

Another way to classify oils is to compare the ratio of *n*-heptane compounds (heptane value) to the ratio of *iso*-heptane compounds (*iso*-heptane value) using the data provided in Thompson (1983) (fig. 6). The heptane and *iso*-heptane values for the oil samples in this study showed a generally positive correlation, but Ordovician oils from *G. prisca*-rich sources elsewhere usually do not follow this trend. Most of the oils from Devonian and younger reservoirs have heptane values of less than 30 and *iso*-heptane values of less than 1.5. The oils from the Ordovician Red River Formation in the Williston basin have heptane values of around 60, but the *iso*-heptane values have an average range of 0.5 to 1.5.

There appears to be a compositional trend in the study oils similar to that seen in figure 5. The Rose Hill samples were most like the Red River Formation oils: they had the highest heptane values (between 55 and 60) and their *iso*-heptane values of around 2.5 were well above the average compositional range. The compositions of the Ben Hur and Swan Creek oil samples trended toward those of the oils from younger reservoirs.

Isotopic Composition of Oil

When the $\delta^{13}C$ values of the aromatic fraction of all the oil samples in this study are plotted against the $\delta^{13}C$ values of the saturated fraction (fig. 7), the locations on the graph fall into the region indicating a marine kerogen source. The isotopic values for oils from the Ordovician Trenton and Black River Groups in the Michigan basin and for extracts of source rocks from the Guttenberg Member of the Decorah Formation (Hatch and others, 1987) are included in figure 7 for comparison purposes.

Oil samples from the Rose Hill field had a wider range of more positive isotopic values, similar to those from the Guttenberg Member. Oil samples from the wells in the fenster in the Rose Hill field and oil samples from the Ben Hur and Swan Creek fields had values which were more similar to those of the Trenton and Black River Group oils from the Michigan basin. The trend was consistent with the compositional trends shown in the plot of aromaticity versus paraffinicity (fig. 5) and in the plot of heptane values versus *iso*-heptane values (fig. 6). The range in isotopic values probably reflects that kerogen $\delta^{13}C$ values in *G. prisca*-enriched source rocks can vary as much as 9.3 per mil within a single sample (Hatch and others, 1987; Mastalerz and others, 2003).

Evidence for Variations in the Depositional Environment of the Source Rocks

Pristane-to-Phytane Ratio and Carbon Preference Index

High percentages of *G. prisca* in kerogen are directly related to depositional environment and produce oils and source rock extracts with dominant odd *n*-alkanes and low amounts of isoprenoids (including pristane and phytane) (Jacobson and others, 1988). A plot of the pristane-to-phytane ratio versus the carbon preference index (CPI) for the oil samples in this study and elsewhere (fig. 8) may reflect (1) differences in the amount of Assemblage A-type and Assemblage B-type kerogen in the source rock from which the study oils were derived and (2) variations in the depositional environment of the source rock.

Although the ratio of pristane to phytane in oil can be influenced by other factors and should be used with caution (Hunt, 1996), it is nevertheless very useful for grouping oils and inferring the lithology and depositional environment of oil source rocks (Hughes and others, 1995; Peters and others, 2005). In general, oils derived from marine-carbonate-dominated kerogen, deposited in water with a higher salinity content and reducing conditions that are far from terrestrial clastic input, have lower pristane-to-phytane ratios (less than or equal to 1) than do oils derived from kerogen that is dominated by continental sediments deposited in relatively lesser reducing conditions (pristane-to-phytane ratios are greater than or equal to 1) (Peters and others, 2005, and references therein). Longman and Palmer (1987) and Jacobson and others (1988) suggested that Assemblage A-type, *G. prisca*-enriched kerogen was deposited in offshore shallow-shelf limestones far from terrigenous clastic input and that Assemblage B-type kerogen was deposited where more shale had accumulated, thus diluting the *G. prisca* signature; therefore, Assemblage A-type kerogen should produce oil with lower pristane-to-phytane ratios than oil derived from sources with more Assemblage B-type kerogen.

Carbon Preference Index

The CPI is calculated so that oil with an odd *n*-alkane predominance has a CPI of greater than 1; the resulting index number can be used to infer the amount of Assemblage A-type, *G. prisca*-rich kerogen in the oil source rock. Oils from the Middle Ordovician reservoirs in the Rose Hill, Ben Hur, and Swan Creek fields appear to have been derived from sediments deposited in an environment that is similar to that of the Red River Formation oils (fig. 8). The Red River oils were derived from marine *G. prisca*-rich carbonate mudstones that were deposited so far from land that the amount of terrestrial sediment is very small (Osadetz and others, 1992). The higher pristane-to-phytane ratios and the lower odd-carbon preference for the Ben Hur and Swan Creek oil samples may reflect more terrestrial input and more mixing with amorphous Assemblage B-type kerogen (Jacobson and others, 1988). The one oil sample in the Swan Creek field known to be from the Knox Group (from the Paul Reed No. 1 well) appeared to be closer in composition to the oils from the Knox Group and Trenton and Black River Group reservoirs in the northern Appalachian basin, which are derived from the Utica Shale (Ryder and others, 1998).

Both the pristane-to-phytane ratios and the CPI values indicated that the oil source rocks for the Ben Hur and the Swan Creek oil samples received more clastic input and may reflect a

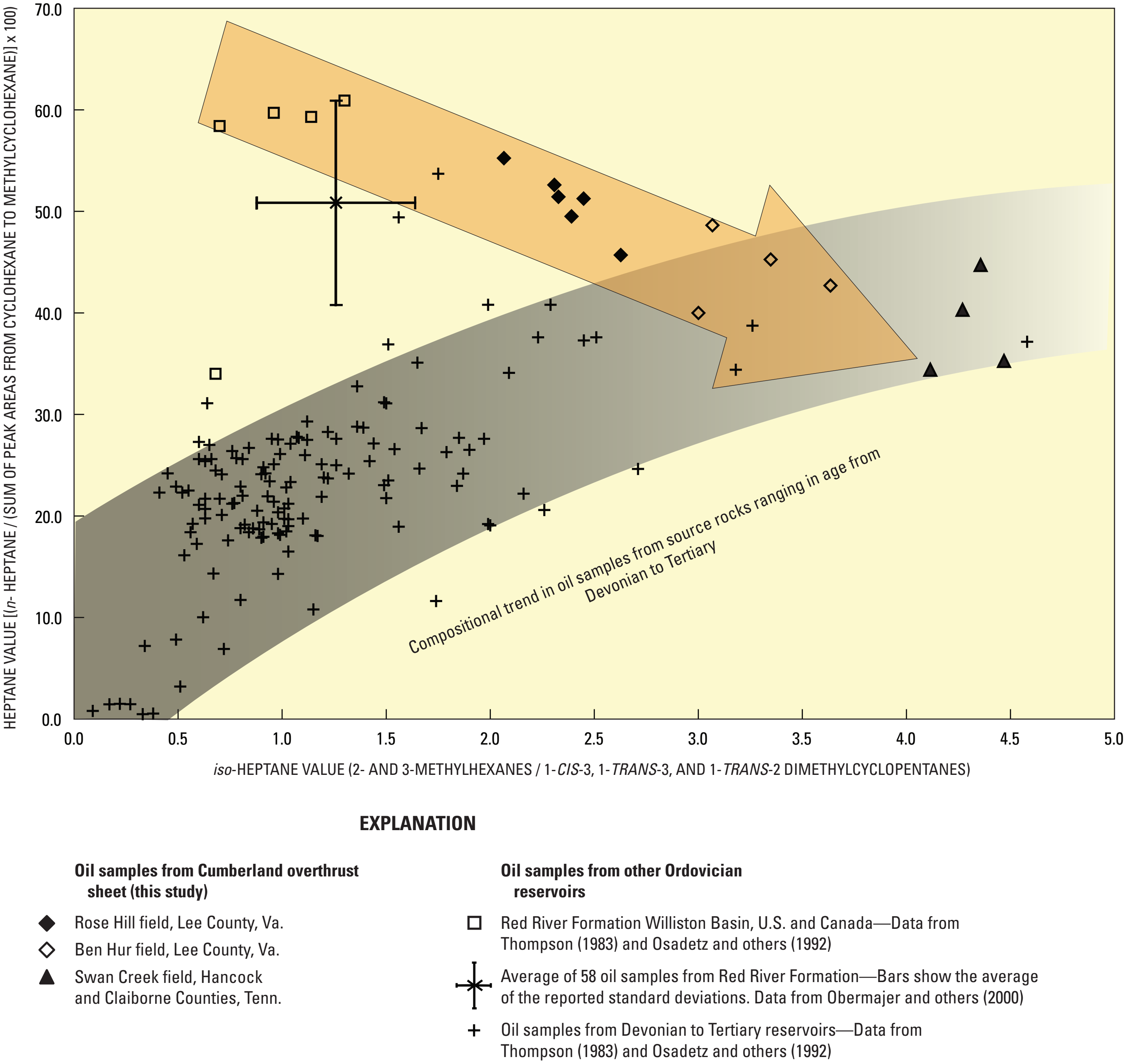


Figure 6. Graph showing *iso*-heptane values versus *n*-heptane values of oil samples from the Cumberland overthrust sheet and (for comparison) of oil samples from Ordovician to Tertiary reservoirs elsewhere in the United States and Canada. The orange arrow indicates that the composition of oil samples from the Cumberland overthrust sheet trends from *Gloeocapsomorpha prisca*-rich oils toward the average compositional trend of oil samples derived from Devonian to Tertiary source rocks.

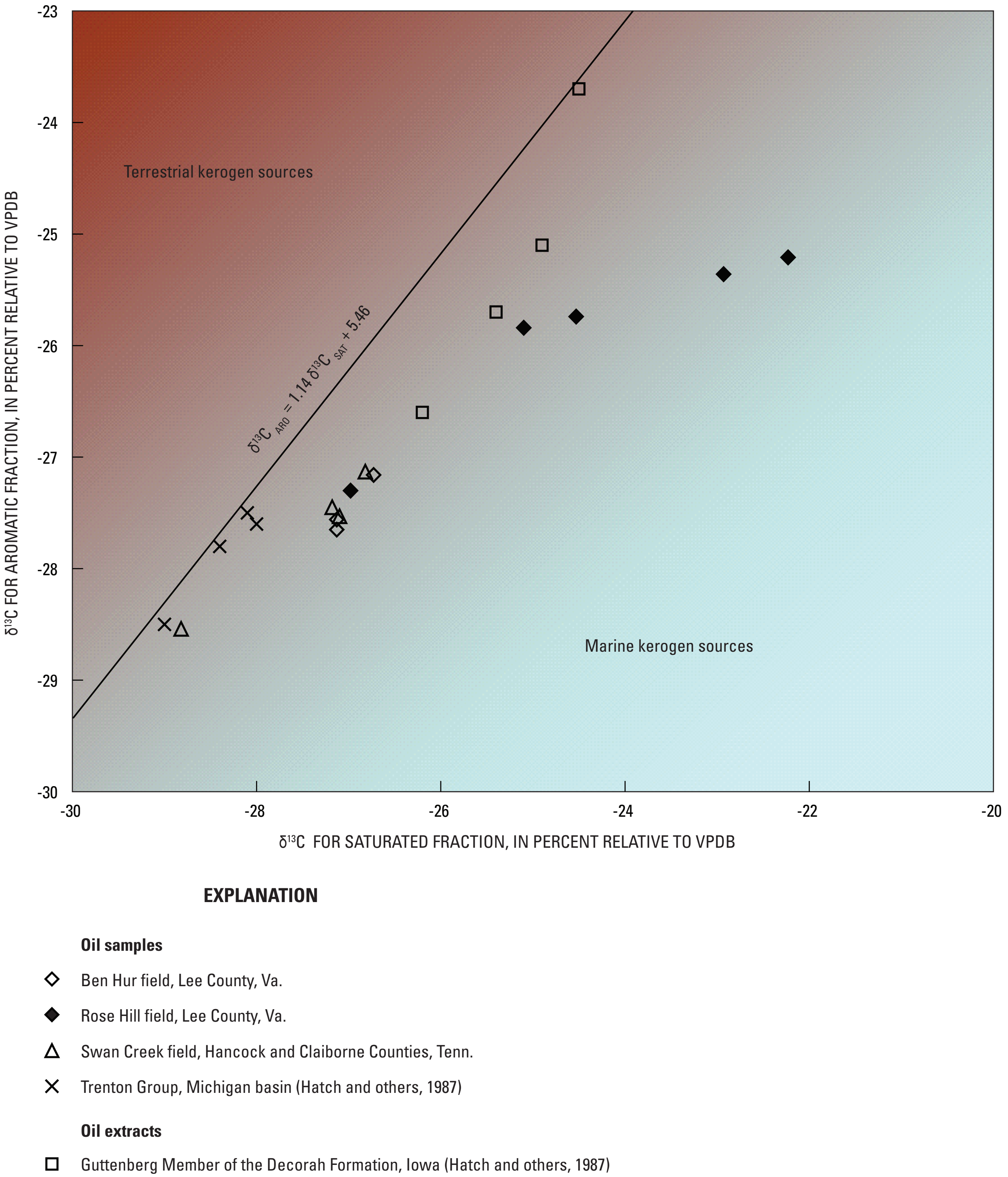


Figure 7. Graph showing the isotopic compositon of carbon ($\delta^{13}C$) of the saturated fraction of the oil versus the $\delta^{13}C$ of the aromatic fraction of the oil from the samples in this study, along with $\delta^{13}C$ values from the saturated and aromatic fractions of oil samples from the Trenton Group in the Michigan basin (Hatch, 1987) for comparison. Sofer (1984) used isotopic analyses of 339 oil samples from around the world, including the United States, to determine the equation of the line best separating oil derived from terrestrial kerogen sources from oil derived from marine kerogen sources. The oil samples plotted in this graph are below that line and therefore are inferred to have originated from a marine kerogen source. Abbreviations are as follows: ARO, aromatic; SAT, saturated; VPDB, Vienna Peedee belemnite standard.

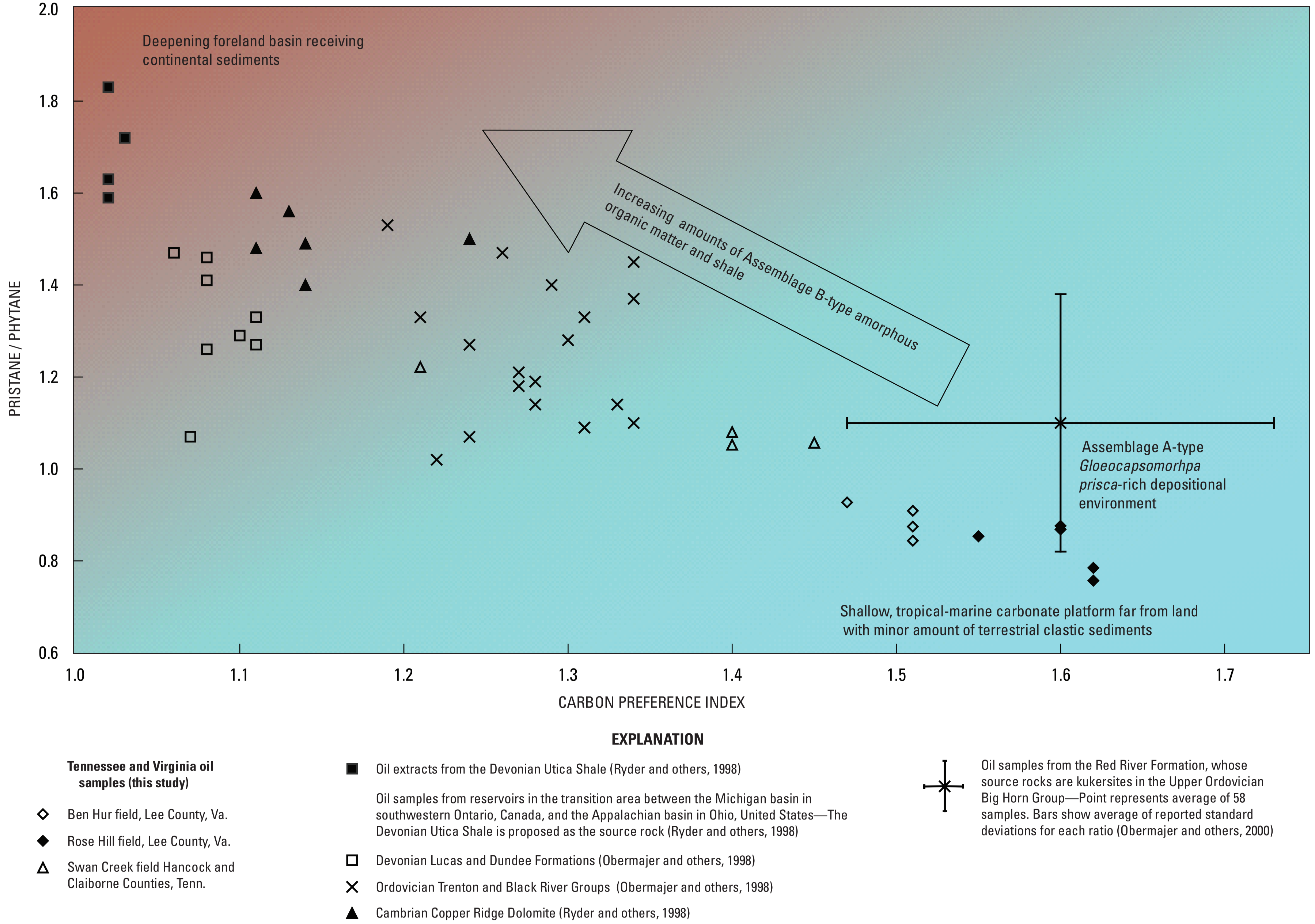


Figure 8. Graph showing the carbon preference index (CPI) versus the pristane-to-phytane ratio for the oil samples in this study and for oil samples from other geographic areas for comparison. The graph can be used to infer the depositional environment of the source rocks for the oil samples. The carbon preference index is calculated using the following formula: $[(n\text{-}C_{14} + n\text{-}C_{16} + n\text{-}C_{18}) / (n\text{-}C_{15} + n\text{-}C_{17} + n\text{-}C_{19}) + (n\text{-}C_{16} + n\text{-}C_{18} + n\text{-}C_{20}) / (n\text{-}C_{15} + n\text{-}C_{17} + n\text{-}C_{19})] \times 0.5$.

shift in depositional facies, as suggested by Jacobson and others (1988) and Mastalerz and others (2003). The shift could have been caused by wind or water currents affecting a large shallow-marine platform, thus dispersing the *G. prisca* remains to deeper offshore depositional areas (Foster and others, 1990). Deposits enriched by *G. prisca* also could have formed in place, such as in algal mats (Foster and others, 1990). The highest TOC values in the Red River Formation are found in biozones where *G. prisca* material is concentrated in burrows (Heinemann and others, 2005). The emergence of highlands to the east of the Cumberland overthrust sheet, which was caused by regional tectonic activity, may have caused changes in the amounts of clastic detritus in the source rocks (Harris and Milici, 1977; Read, 1980; Milici and others, 2006). The source rocks in the Rose Hill field may have been deposited at or near where they formed, thereby retaining their more pure Assemblage A-type, *G. prisca*-rich profile compared with the Ben Hur and Swan Creek source rocks.

Natural Gas Geochemistry

Methane

In this study, the methane contents in the gas samples increased with depth (fig. 9). The gas samples from the shallowest wells (the wells in the fensters) had the least methane relative to other hydrocarbons. The samples from the deepest wells in the Swan Creek field, which produced gas from the Knox Group, had the highest methane content. This was also true for the deepest wells in the Ben Hur and Rose Hill fields.

The stable isotopic composition of methane in the gas samples is shown in figure 10. The samples from the shallowest wells (in the fensters) had the most negative values of δ^2H and $\delta^{13}C$. The values become more positive with depth in other wells. The samples from the deepest wells in the Swan Creek field had the most positive methane isotopic values. In summary, the deepest wells in the Cumberland overthrust sheet produce gas with the highest methane concentrations and with the most positive isotopic compositions.

Ethane and Propane

The trend in $\delta^{13}C$ values for ethane and propane (fig. 11) is different from that for methane; therefore, depth was probably not a factor in the range of these values. All the gas samples plot in a range associated with early mature oil generation. The Rose Hill gas samples plotted in a group closest to the maturity trend line, and the Knox Group gas samples are in a group farthest away. The wells in the fensters and the wells producing gas from the Ordovician reservoirs in the Swan Creek and Ben Hur fields plotted in between these locations. In figure 11, the deviation away from the maturity (vitrinite reflectance, or $\%R_o$) trend line suggests that the maturity of the kerogen source was not the determining factor in the composition of the gas with the higher hydrocarbon numbers. Whiticar (1994) infers this to be a result of mixing of gases from different sources. Nevertheless, the variation in the isotopic composition of the gas samples in this study was consistent with the isotopic range found in *G. prisca*-enriched kerogen (Reed and others, 1986; Hatch and others, 1987; Ludvigson and others, 1996; Mastalerz and others, 2003).

Natural Gas Plots

Another way to relate the isotopic composition of gas to a source and process is to compare the $\delta^{13}C$ composition of each component to the reciprocal of the number of carbons in the component, as shown in figures 12 and 13. This relation is based on theoretical concepts of the kinetic isotope effect that occurs during the thermal breakdown of high molecular weight hydrocarbons to low molecular weight gas (Chung and others, 1988; Rooney and others, 1995). An

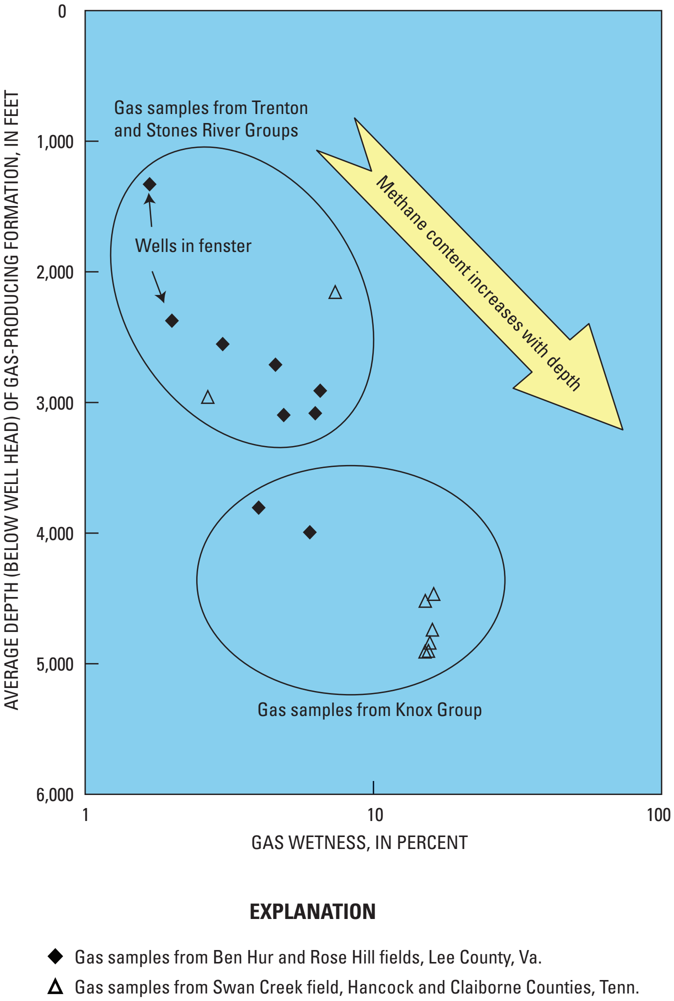


Figure 9. Graph showing the ratio of gas wetness (methane ÷ (methane + sum of heavier hydrocarbon gases), in percent) versus the average depth below well head of a gas-producing formation for gas samples from the Cumberland overthrust sheet. The graph shows that methane concentrations increase with depth.

important consequence of this relation is that the isotopic compositions of gas from a single source should plot on a straight line between the isotopic compositions of methane and the source. Deviations from a straight thermal cracking line suggest that something other than thermal cracking of higher hydrocarbons is the determining factor in the isotopic composition of the gas.

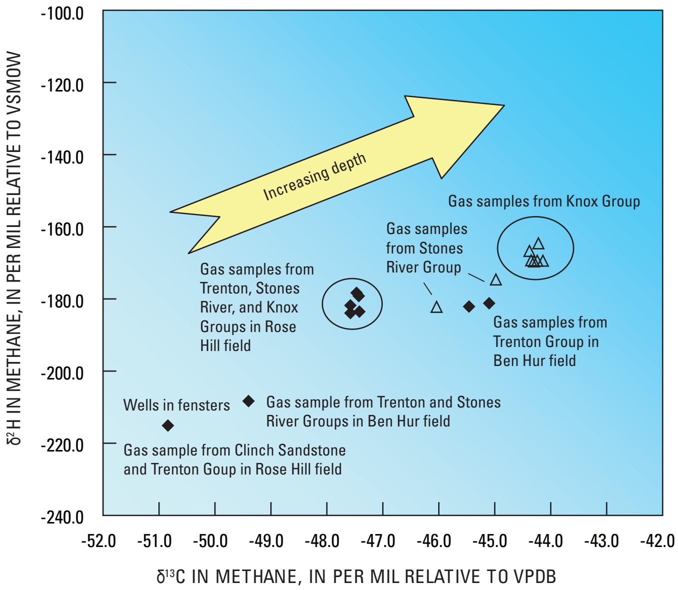
Natural Gas From the Ben Hur and Rose Hill Fields

The gas samples from the reservoirs in the "Stones River" formations and Trenton Limestone reservoirs in the Ben Hur and Rose Hill fields in Lee County, Va., have different profiles, which suggest that the gas had different sources in each reservoir (fig. 12). The gas samples from the reservoirs in the "Stones River" formations exhibit a deviation from a straight thermal cracking line, with both ethane and methane isotopically more positive than the corresponding gas samples from reservoirs in the Trenton Limestone. The gas samples from the reservoirs in the Trenton Limestone also do not fall on a straight line; instead, they form a concave-downward pattern, which suggests that the isotopic compositions of ethane and propane are more positive than if they had been generated and trapped without mixing or alteration. The slight downward deflection in the $\delta^{13}C$ values of methane in each reservoir is interpreted to be the result of mixing with biogenically generated methane. Extrapolation of the isotopic compositions of the gas samples from the Ben Hur and Rose Hill fields to possible kerogen compositions yields estimates of about -23 to -24 per mil, which is at the more positive end of the range of kerogen values for *G. prisca*-enriched rock samples reported by Hatch and others (1987) and Mastalerz and others (2003).

Natural Gas From the Swan Creek Field

The natural gas plots for the gas samples from the Stones River Group in the Swan Creek field in Hancock and Claiborne Counties, Tenn., have profiles that are almost straight, which indicates that simple thermal cracking of higher hydrocarbons is the major factor in the gas composition (fig. 13). The exception is methane, where the slight downward deflection in $\delta^{13}C$ suggests some mixing with biogenically generated methane. Extrapolation to possible kerogen source compositions for these gas samples yields compositions of about -23 to -24 per mil, which is similar to samples from from the Ben Hur and Rose Hill fields.

The natural gas plots for the eight gas samples from the Knox Group rocks in the Swan Creek field are almost

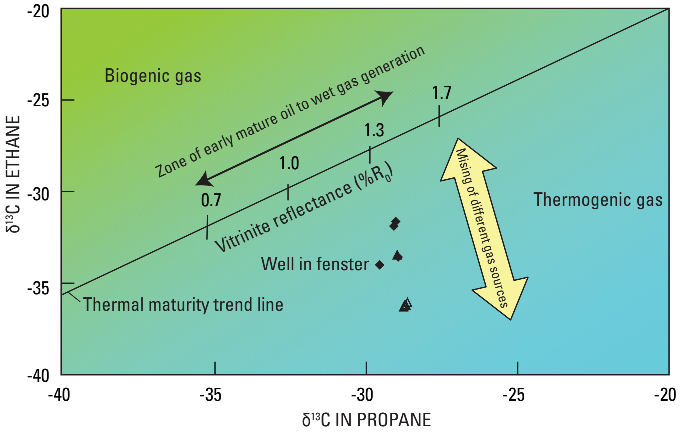


EXPLANATION

◆ Gas samples from Ben Hur and Rose Hill fields, Lee County, Va.

△ Gas samples from Swan Creek field, Hancock and Claiborne Counties, Tenn.

Figure 10. Graph showing the isotopic composition of carbon ($\delta^{13}C$) in methane relative to the Vienna Peedee belemnite (VPDB) standard versus the isotopic composition of hydrogen (deuterium) (δ^2H) in methane relative to the Vienna standard mean ocean water (VSMOW) for gas samples from the Cumberland overthrust sheet. The graph shows that values increase (become less negative) with depth.



EXPLANATION

◆ Gas samples from Ben Hur and Rose Hill fields, Lee County, Va.

△ Gas samples from Swan Creek field, Hancock and Claiborne Counties, Tenn.

Figure 11. Graph showing the isotopic composition of carbon ($\delta^{13}C$) in propane versus that in ethane for the gas samples from the Cumberland overthrust sheet. The vitrinite reflectance (maturity) values of the source rocks were calculated from the difference between isotopic compositions of carbon in propane and ethane in their produced gases by Faber and Stahl (1987). The gas samples in this study are inferred to be from source rocks of similar maturity. Deviations from the maturity trend line were inferred by Whiticar (1994) to indicate mixing of gas sources.

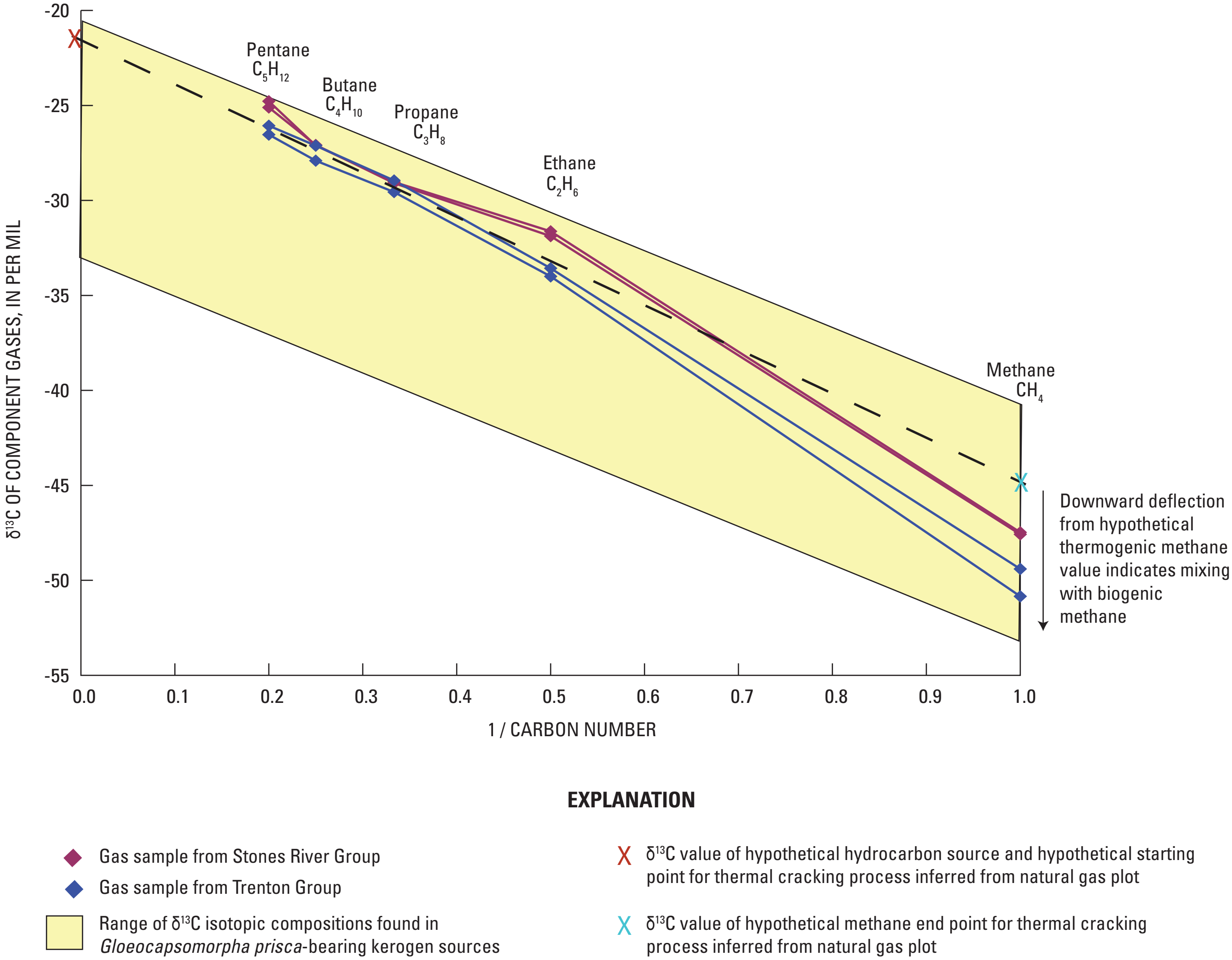
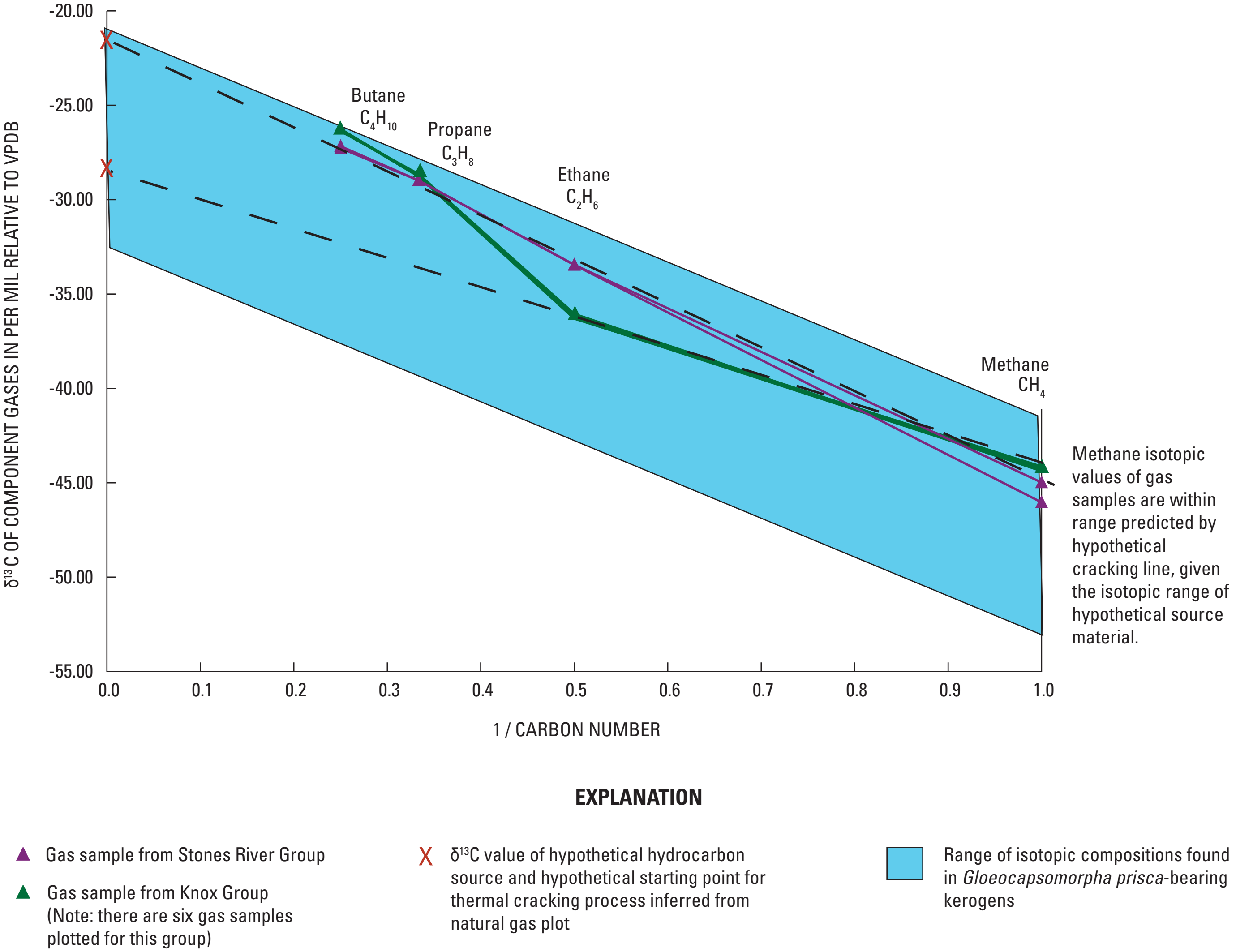


Figure 12. Graph showing the reciprocal of the component carbon number versus the isotopic composition of carbon ($\delta^{13}C$) in the hydrocarbon gas for four gas samples from Lee County, Va. (Chung and others, 1988). The gas samples from the "Stones River" formations and the Trenton Limestone wells are slightly different and may be mixed with some biogenic methane. The dashed line represents the hypothetical line of isotope values generated by thermal cracking (thermogenic gas). The shaded area shows the range of possible straight cracking lines, given the isotopic range of the inferred source rock. The range of $\delta^{13}C$ values found in Ordovician *Gloeocapsomorpha prisca*-bearing kerogen sources is -22.6 per mil to -33.2 per mil (Hatch and others, 1987; Mastalerz and others, 2003). VPBD, Vienna Peedee belemnite standard.

identical and appear as a single line (fig. 13). There is a downward deflection toward more negative values for ethane relative to propane. The carbon isotope values for methane in the Knox Group samples are more positive than the values for the Stones River Group samples, which may have been mixed with a small amount of biogenic methane. The range of possible thermal cracking lines for the Knox Group samples (indicated by the shaded area) leads to a much wider range of extrapolated carbon isotope values for kerogen sources, but the range (-22.6 to -33.2 per mil) is still consistent with that found for *G. prisca*-enriched source rocks by Hatch and others (1987) and Mastalerz and others (2003). The isotopic compositions of the gas samples from all three fields show evidence that a simple maturation trend has been altered, with the Knox Group samples exhibiting the strongest evidence of mixing from more than one isotopic source.

Conclusions

The oil from the Rose Hill and Ben Hur fields in Lee County, Va., and the Swan Creek field in Hancock and Claiborne Counties, Tenn., are from a marine-algal source



Methane isotopic values of gas samples are within range predicted by hypothetical cracking line, given the isotopic range of hypothetical source material.

Figure 13. Graph showing the reciprocal of the component carbon number versus the isotopic composition of carbon (δ^{13}C) in the hydrocarbon gas for four gas samples from the Swan Creek field, Hancock and Claiborne Counties, Tenn. (Chung and others, 1988). The graph shows that two samples from the Stones River Group reservoirs form nearly straight lines that are almost parallel to a theoretical thermal cracking line. The six gas samples from Knox Group reservoirs appear as a single line on the graph. The range of δ^{13}C values found in Ordovician *Gloeocapsomorpha prisca*-bearing kerogen sources is -22.6 per mil to -33.2 per mil (Hatch and others, 1987; Mastalerz and others, 2003). VPDB, Vienna Peedee belemnite standard.

enriched in Assemblage A-type, *G. prisca*-enriched kerogen. The differences in the oil compositions are probably due to localized differences in the specific marine depositional facies that was enriched in *G. prisca*. The environments range from a more carbonate-rich environment in the Rose Hill field to an environment with more shale and more mixing of Assemblage A-type kerogens with Assemblage B-type kerogen in the Ben Hur and Swan Creek fields.

The associated gases from all three fields have geochemical characteristics consistent with those of the oils. The gases are from sources with variable isotopic signatures within the same range found in *G. prisca*-enriched source rocks elsewhere. Gases from the Cambrian to Lower Ordovician Knox Group in the Swan Creek field are different from gases in the Middle and Upper Ordovician reservoirs in all three fields, which is evidence of a source with a broader isotopic range. The gas profiles from each reservoir within and between the fields are different, which suggests that the source for the gases may be contained within each reservoir. There is evidence of some biogenic methane in the Ben Hur and Rose Hill gases and in the gases from the Stones River Group rocks in the Swan Creek field.

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Appendix A.—Individual Gas Chromatographic Profiles of the Whole Crude Oils

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Individual gas chromatographic profiles of the whole crude oils are shown in figures A1 through A14. Representative biomarker fragmentograms and an aromatic fraction chromatogram are shown in appendix B, figure B1.

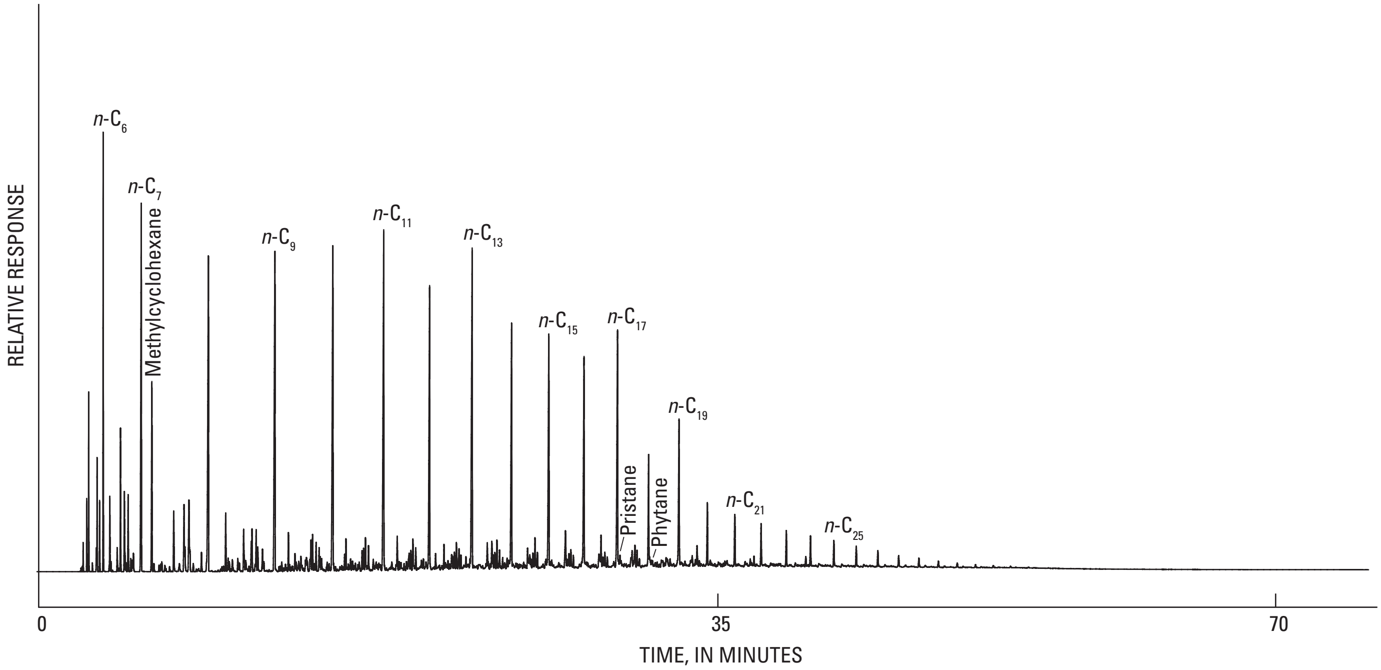

Figure A1. Gas chromatogram for whole crude oil from the No. 108 well, where n-C_x indicates a normal alkane with x number of carbons.

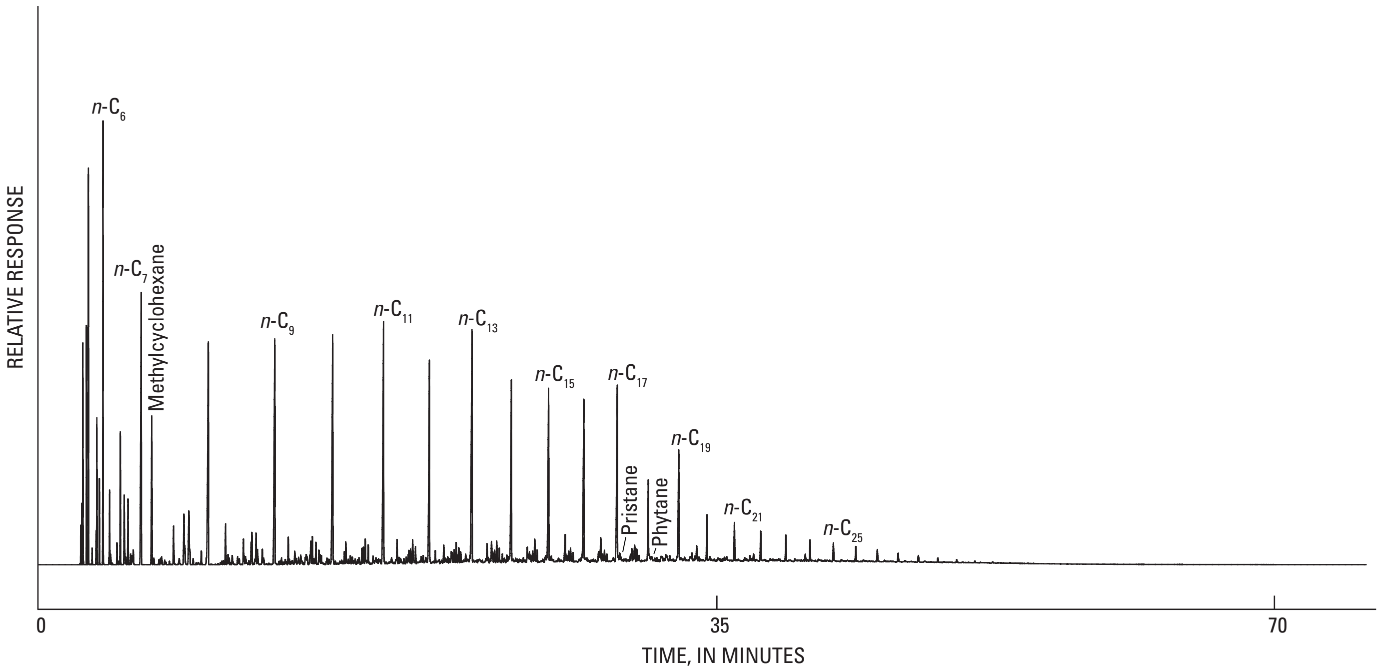

Figure A2. Gas chromatogram for whole crude oil from the James Dean No. 1 well, where n-C_x indicates a normal alkane with x number of carbons.

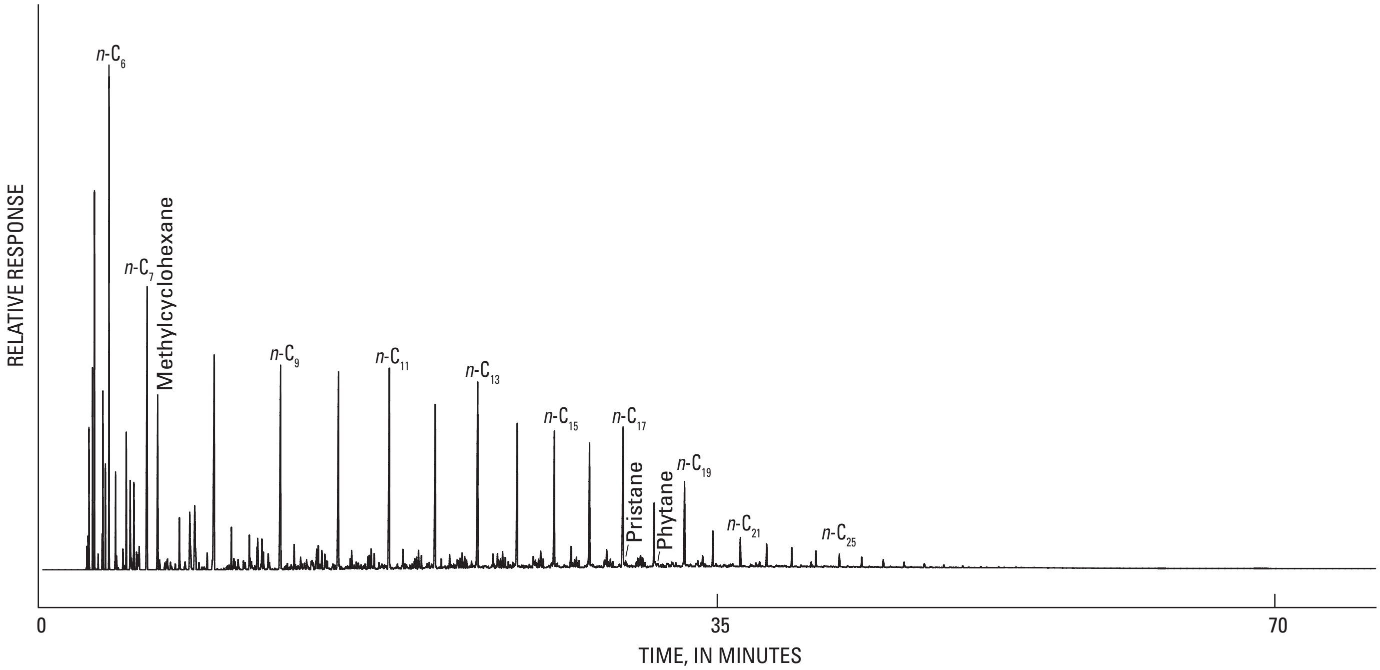

Figure A3. Gas chromatogram for whole crude oil from the Yeary No. 1 well, where n-C_x indicates a normal alkane with x number of carbons.

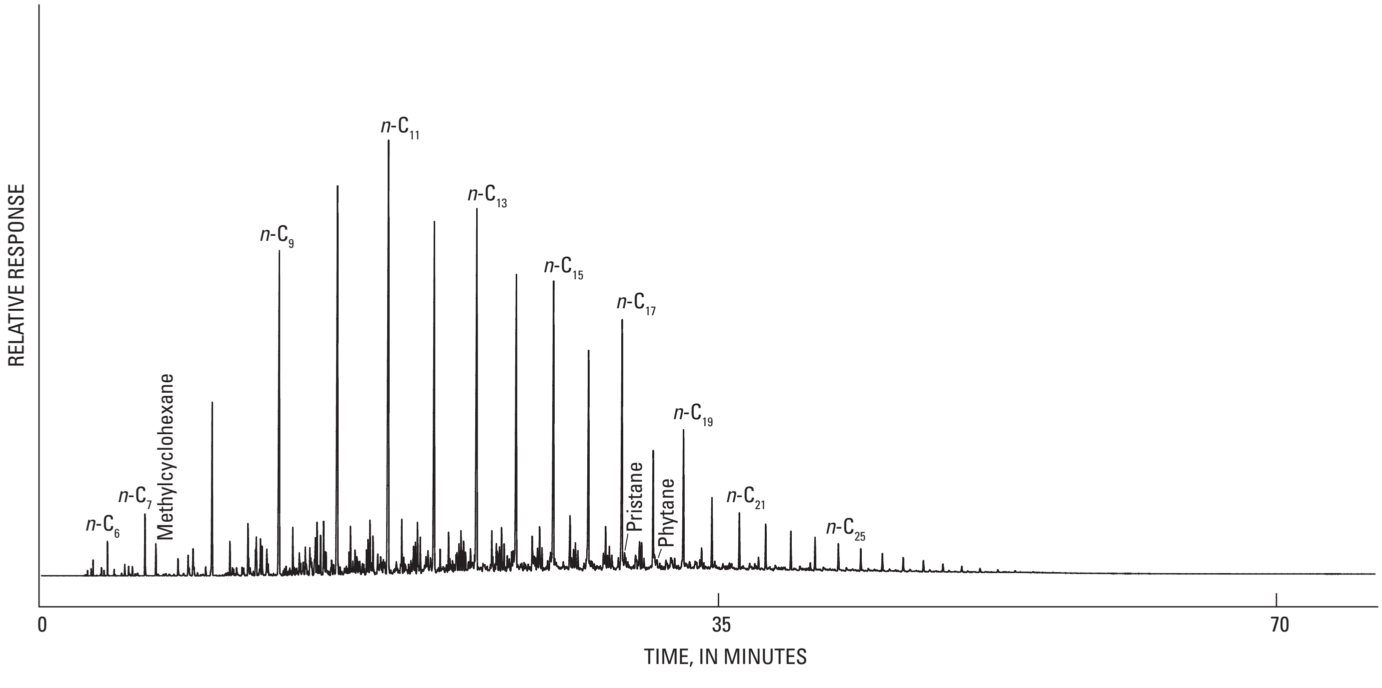

Figure A4. Gas chromatogram for whole crude oil from the No. 8709 well, where n-C_x indicates a normal alkane with x number of carbons.

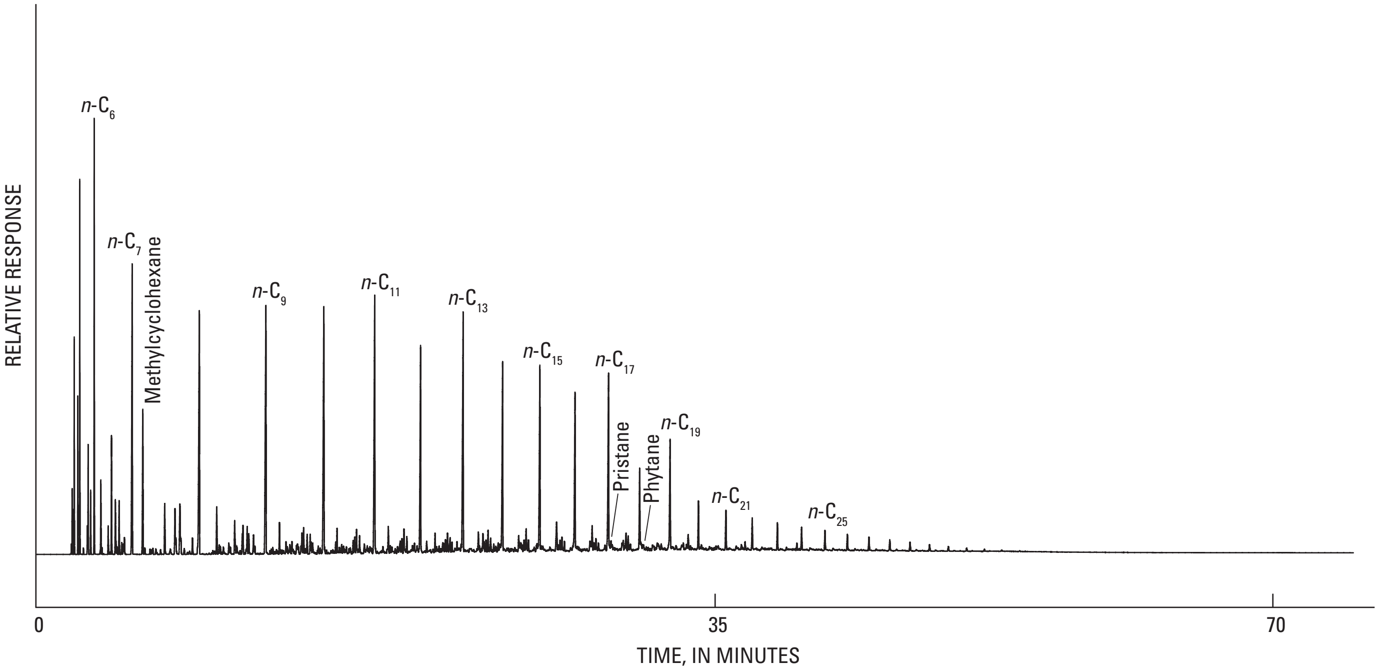

Figure A5. Gas chromatogram for whole crude oil from the PO–1 well, where n-C$_x$ indicates a normal alkane with x number of carbons.

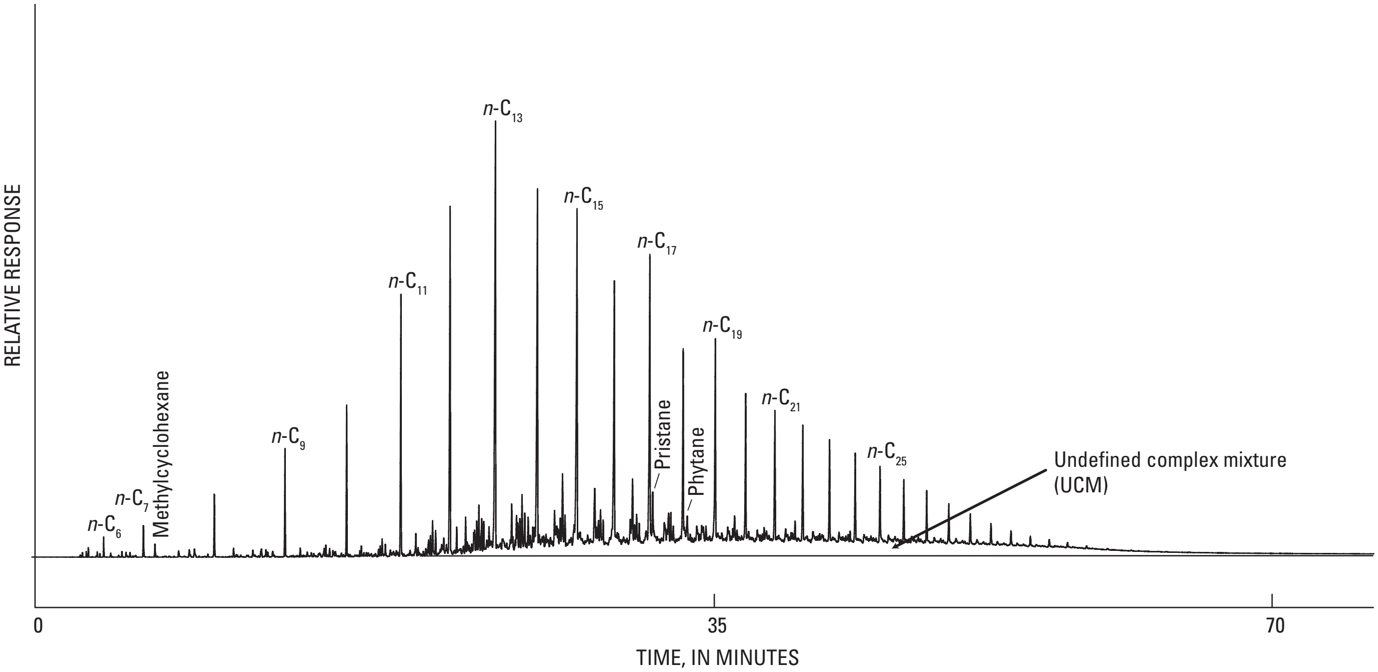

Figure A6. Gas chromatogram for whole crude oil from the Morgan Hensley No. 1 well, where n-C$_x$ indicates a normal alkane with x number of carbons.

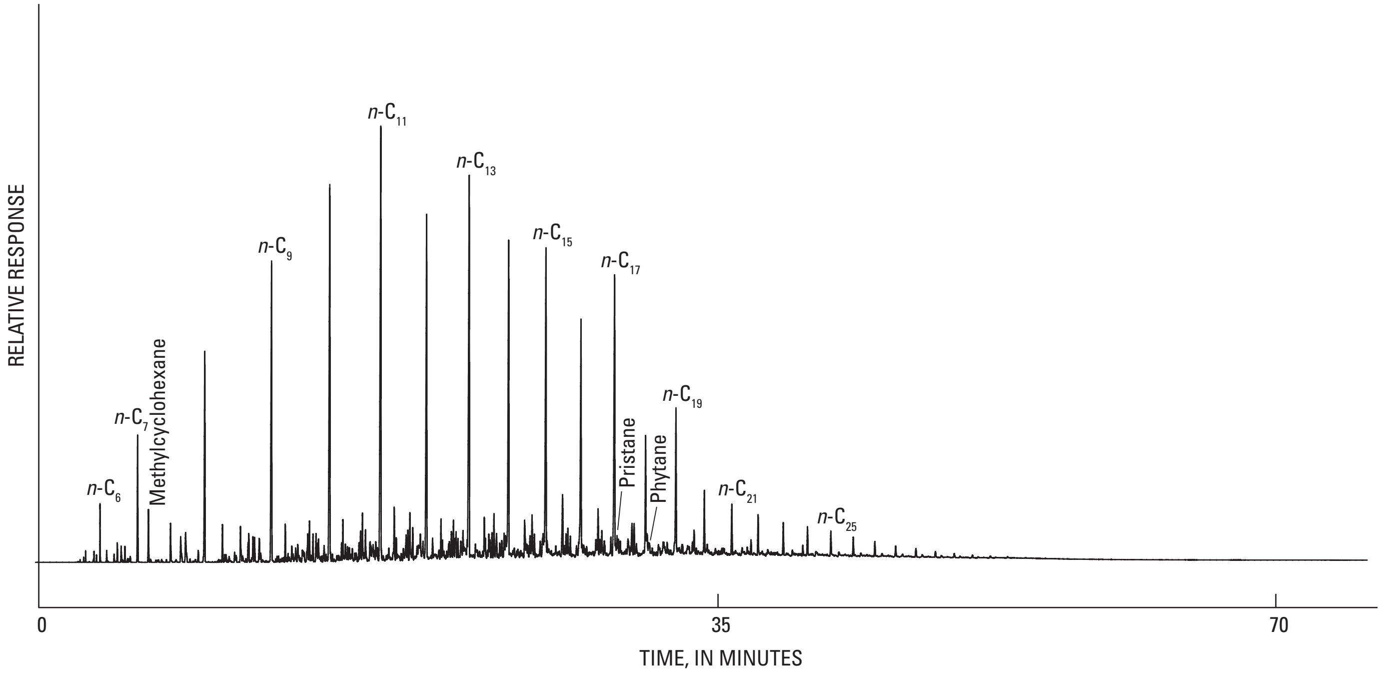

Figure A7. Gas chromatogram for whole crude oil from the No. 8708 well, where n-C_x indicates a normal alkane with x number of carbons.

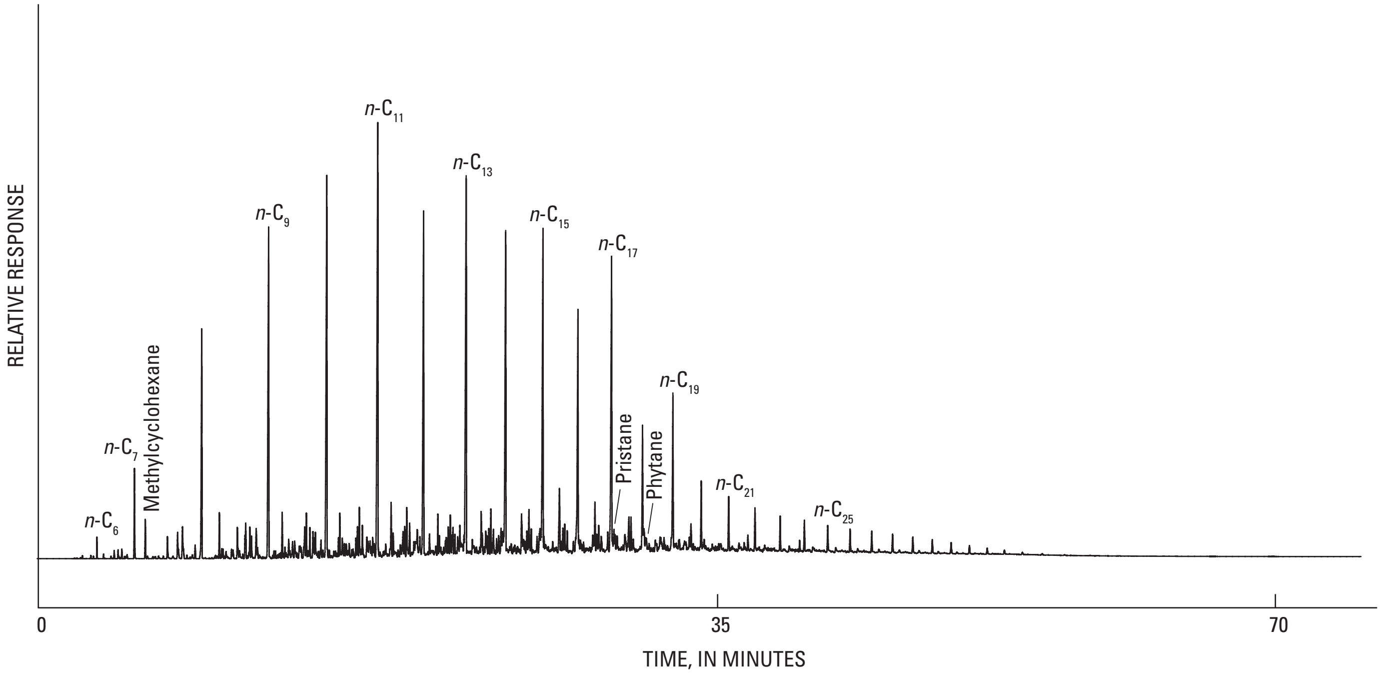

Figure A8. Gas chromatogram for whole crude oil from the No. 1001 well, where n-C_x indicates a normal alkane with x number of carbons.

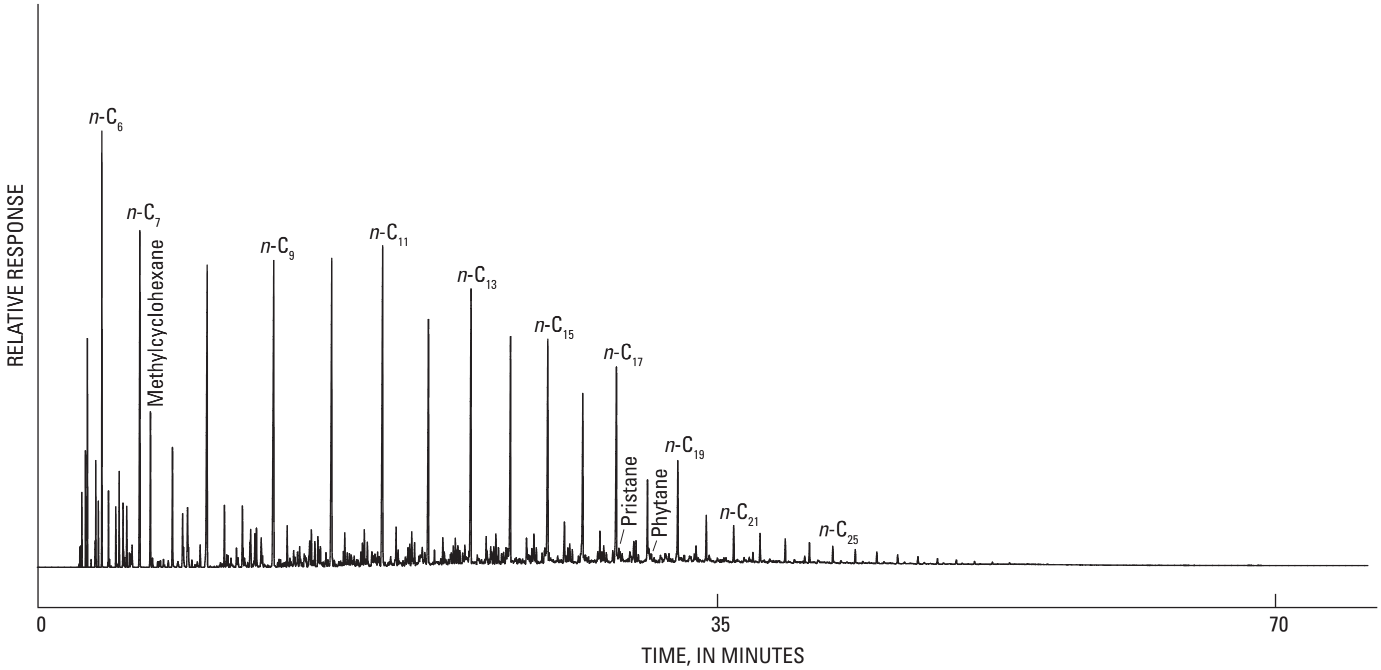

Figure A9. Gas chromatogram for whole crude oil from the No. 1000 well, where n-C_x indicates a normal alkane with x number of carbons.

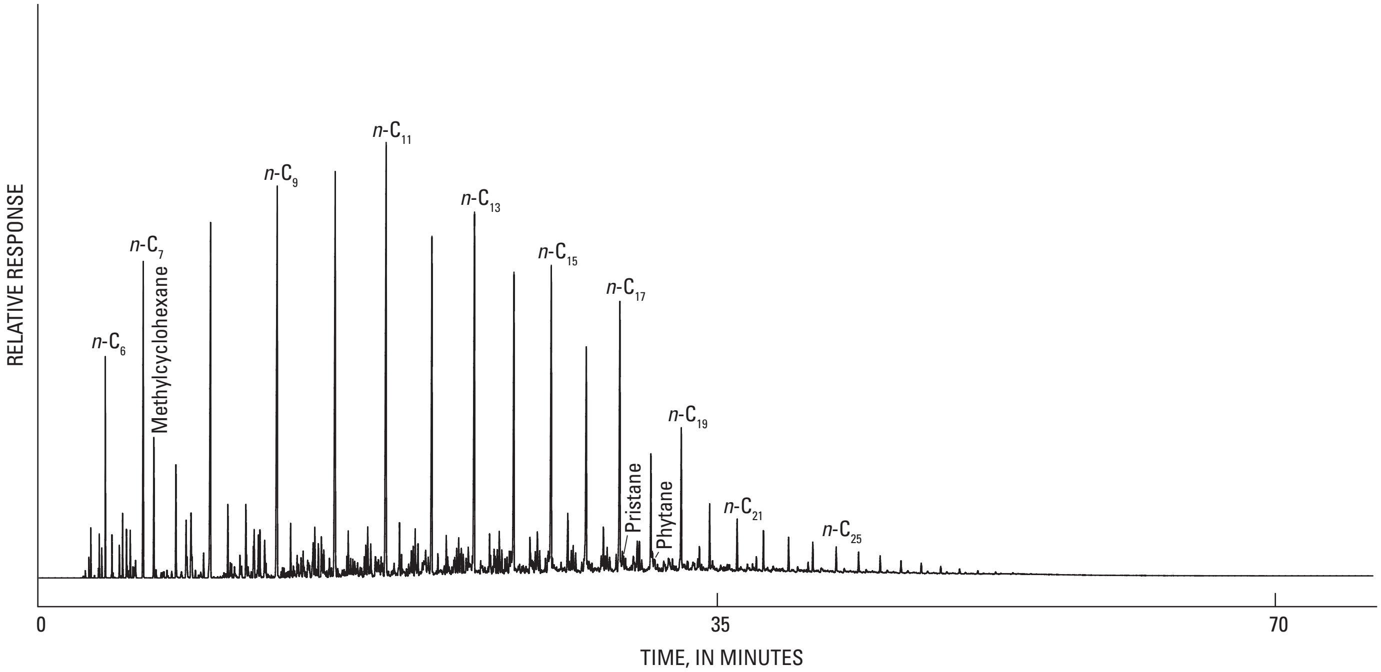

Figure A10. Gas chromatogram for whole crude oil from the Sarah Hensley No. 1 well, where n-C_x indicates a normal alkane with x number of carbons.

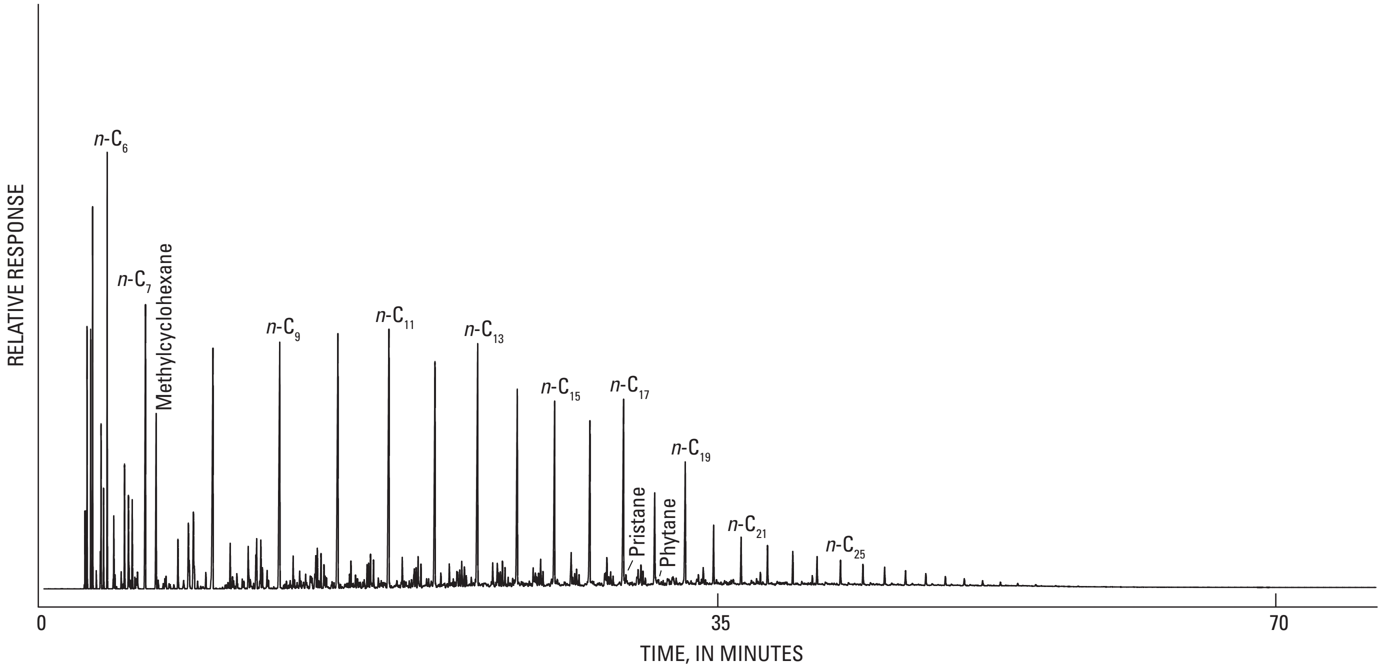

Figure A11. Gas chromatogram for whole crude oil from the Paul Reed No. 2 well, where *n*-C_x indicates a normal alkane with *x* number of carbons.

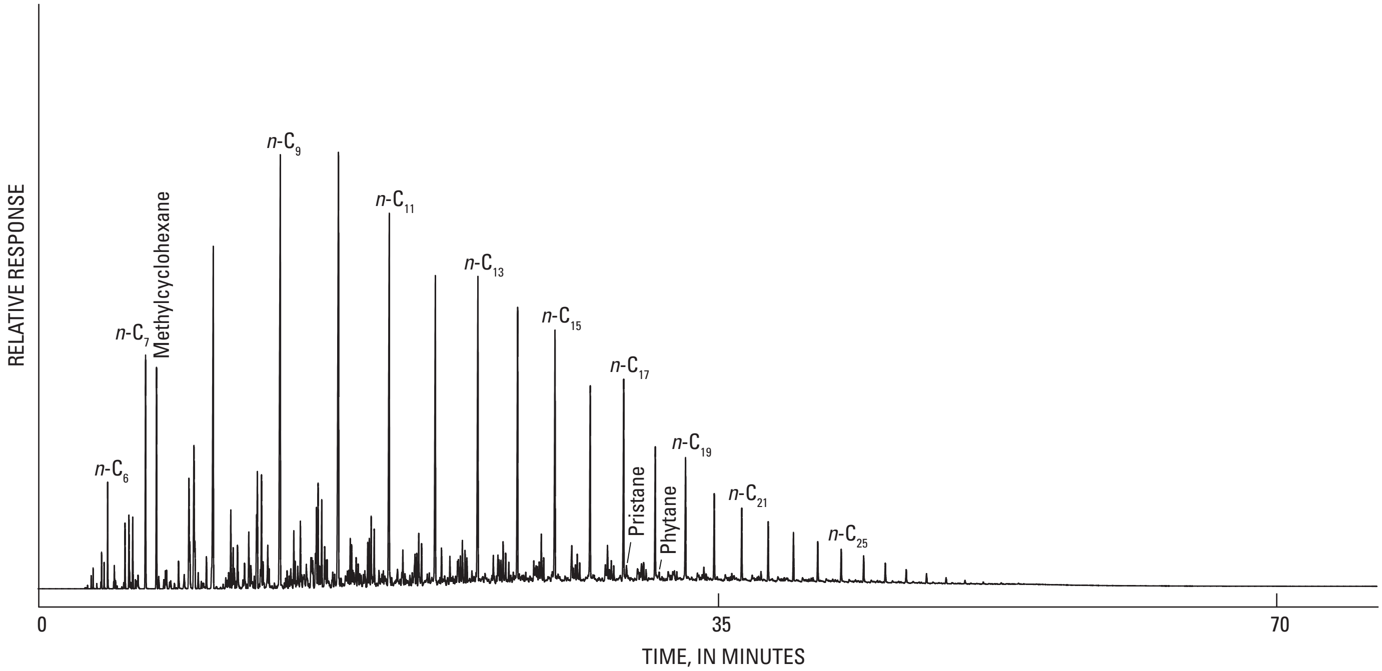

Figure A12. Gas chromatogram for whole crude oil from the Paul Reed No. 1 well, where *n*-C_x indicates a normal alkane with *x* number of carbons.

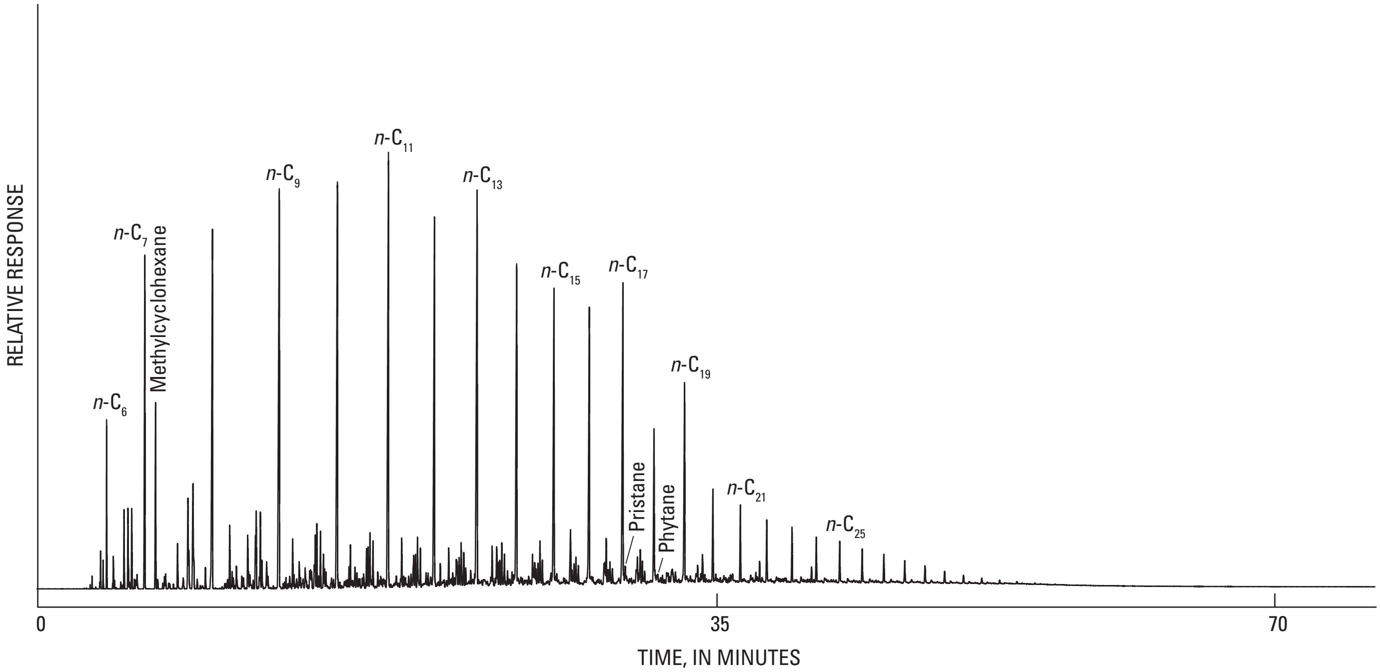

Figure A13. Gas chromatogram for whole crude oil from the Gary Patton No. 1 well, where n-C_x indicates a normal alkane with x number of carbons.

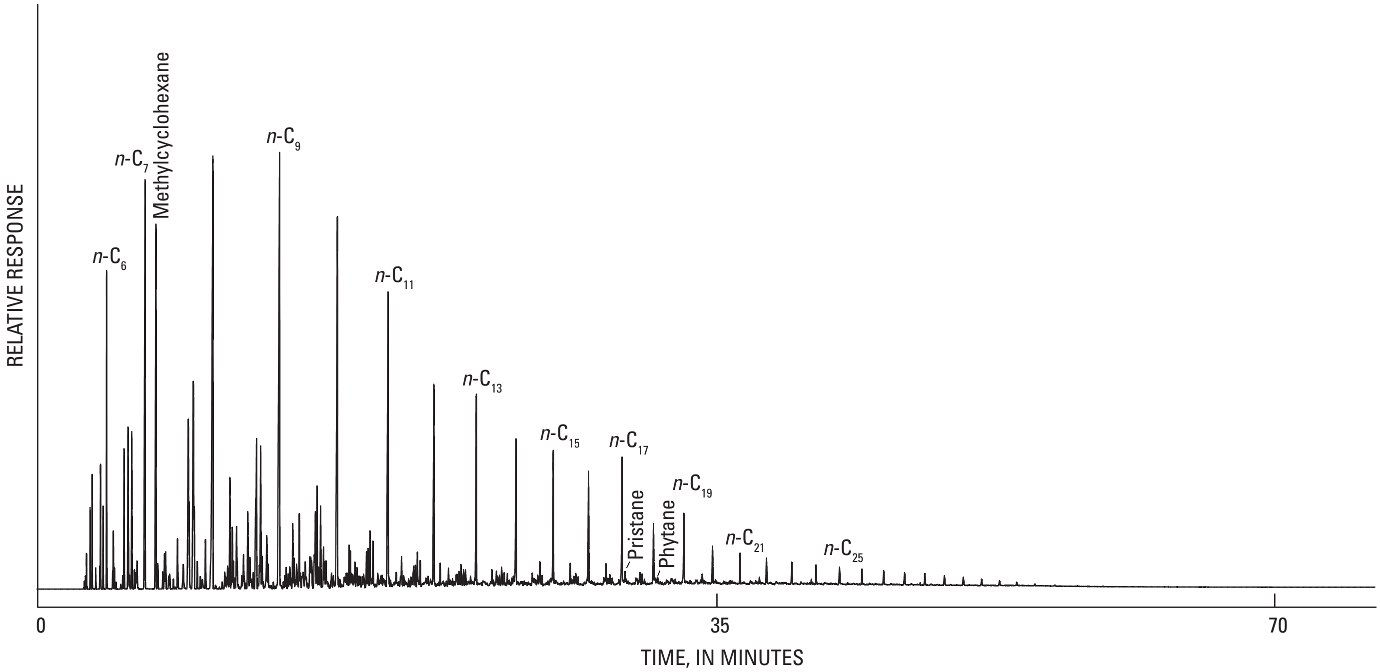

Figure A14. Gas chromatogram for whole crude oil from the Stephen Lawson No. 2 well, where n-C_x indicates a normal alkane with x number of carbons.

Appendix B.—Representative Biomarker Profiles

Representative biomarker fragmentograms and an aromatic fraction chromatogram are shown in figure B1.

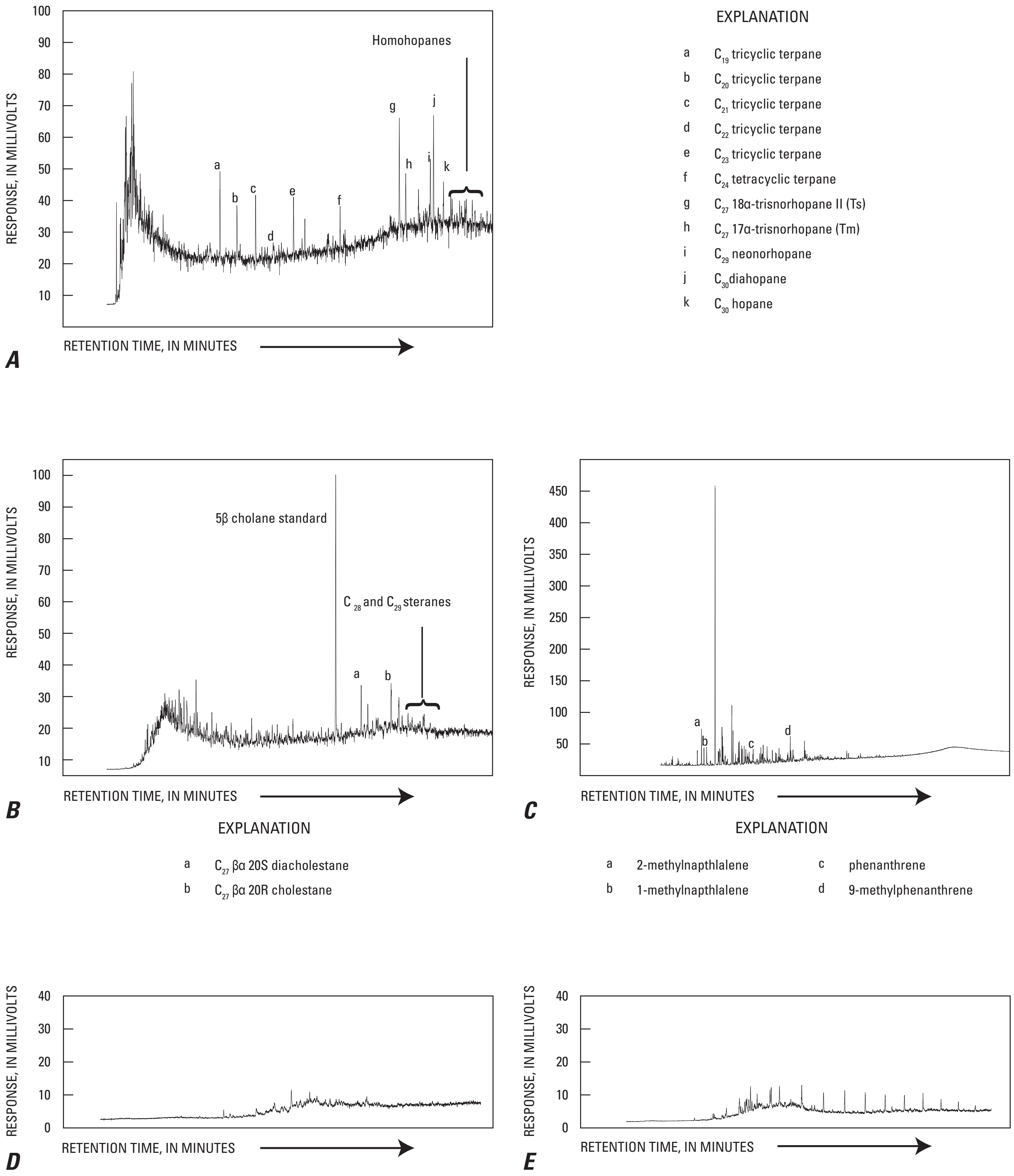

Figure B1. Representative biomarker profiles for oil samples from the James Dean No. 1 well in the Ben Hur field, Lee County, Va. Producing formation is Trenton Limestone. Average depth of producing formation is 2,374 ft. *A*, Terpane mass fragmentogram, scanning range mass-to-charge ratio (*m/z*) is 191. *B*, Sterane mass fragmentogram, scanning range *m/z* is 217. *C*, Aromatic fraction chromatogram. *D*, Triaromatic sterane mass fragmentogram, scanning range *m/z* is 231. *E*, Monoaromatic sterane mass fragmentogram, scanning range *m/z* is 253.