Chapter 7.

Cambrian and Ordovician Hydrocarbon Geochemistry

D.C. Harris
Kentucky Geological Survey

Introduction

The presence of hydrocarbon source rocks in Cambrian sub-Knox Group sedimentary rocks of the Appalachian Basin has been debated for years. Numerous shows of oil and gas in sub-Knox Group rocks have suggested that mature source rocks exist, but the lack of commercial production left doubt as to whether source rocks were rich enough to have formed significant accumulations. Limited production in the 1970's and 1980's, and more significant commercial production from the Homer Field in Elliott County, Ky. and a nearby well in Lawrence County, Ky. in the 1990's indicate that economic Cambrian reservoirs are present in the Appalachian Basin, outside of Ontario, Canada. Data available for the Homer Field from 1997 through 2000 indicate a minimum of 1.8 BCF of gas has been produced (this number does not include data for the first 3 years of production).

Natural gas and condensate in Conasauga/Rome reservoirs is most easily explained as being derived from Cambrian source rocks, but previous studies did not identify source rocks with significant organic content (Ryder and others, 1998). An alternative model would involve downward or lateral migration of hydrocarbons from more deeply buried Ordovician post-Knox source rocks or from the Knox Group, from deeper in the Appalachian Basin to the east. through several thousand feet of carbonates. There is no evidence to suggest that downward or long-range lateral migration has occurred. Organic matter in sufficient abundance to generate commercial hydrocarbons is known to occur in Cambrian and even Precambrian rocks in other basins. Examples include the Precambrian Nonesuch Formation in Michigan (Elmore and Daniels, 1988) and the Cambrian Deadwood Formation reservoirs in the Williston Basin.

Previous studies in the Appalachian Basin have documented probable hydrocarbon source rocks of Late Ordovician age, but indicated lean, low organic content in Cambrian rocks (Ryder and others, 1998). Webb (1980, p. 28) reported poor source quality, with total organic content ranging from 0.9 to 1.5 mg/g (0.09 to 0.15%) for the Cambrian Nolichucky Shale in the Rome Trough area. The source of Webb's data is unknown, and details on the type of analysis and location of the samples were not given.

The goal of the geochemical part of this study was to compile a database of published and unpublished geochemical analyses of Cambrian pre-Knox Group rocks and produced hydrocarbons. Very little geochemical data has been published for the Cambrian in the Appalachian Basin, consisting primarily of work by the U.S. Geological Survey (Ryder and others, 1991; 1998). These data have been compiled in a computer spreadsheet file (Microsoft Excel format). We had hoped to also include data contributed from industry

sources, and requested data from Texaco and Exxon, two of the larger companies that drilled Cambrian wells in the Rome Trough. Neither company responded to requests for this type of data. As a result we were only able to include published data from Ryder and others (1998), Harris and Baranoski (1996), Cole and others (1987), and Webb (1980).

Although not originally planned as a part of this project, we were able to obtain a number of new geochemical analyses though our collaboration with Bob Ryder, Bob Burruss, and Robert Milici at the U.S. Geological Survey (Reston). This work included analysis of natural gas and condensate samples from the Homer Field (Elliott County, Ky.), and a one-well field in Lawrence Co., Ky. The data also include Rock Eval pyrolysis of potential source rock samples from various Cambrian cores in the study area. The Elliott and Lawrence County gas and condensate samples were collected in June 1999, by Bob Burruss and Bob Ryder of the USGS, along with Dave Harris and Jim Drahovzal of KGS. Equitable Resources subsequently gave permission for the USGS to release this data to the consortium. In addition, a few samples were analyzed for vitrinite reflectance, to provide data on thermal maturity. Figure 7-1 shows the location and type of geochemical data collected. All of the new data collected by the USGS is included in the geochemical data file included on the project CD. This includes numerical Rock Eval and gas analysis data, and scanned images of all gas chromatograms from the condensate samples.

SOURCE ROCK DATA

While studies of Ordovician hydrocarbons and source rocks from a variety of areas have been published (Reed and others, 1986; Cole and others, 1987; Longman and Palmer, 1987; Fowler, 1992; Guthrie and Pratt, 1995; Obermajer and others, 1999), data from Cambrian rocks, particularly from the Rome Trough are limited. For this report we have included data published by Ryder and others (1998), and Cole and others (1987). These data are summarized in Table 7-1.

Published Data

The quality of potential hydrocarbon source rocks is commonly determined using a pyrolysis technique called Rock-Eval. Peters (1986), Tissot and Welte (1978) and Hunt (1996) give good overviews of this technique. We have also included a document from Humble Geochemical, Inc. that discusses the interpretation of Rock-Eval data on the project CD-ROM. This file is in Adobe Acrobat format (PDF). Rock-Eval involves analysis of a whole rock sample, and is faster than other methods that involve isolation of organic matter from the rock. Rock-Eval involves heating a powdered sample through a range of temperatures up to 550ºC. During this process, any hydrocarbons already present in the sample are volatilized and measured as the S_1 peak. Heating the sample to higher temperatures results in pyrolysis of kerogen in the sample to produce hydrocarbons (measured as the S_2 peak) and CO_2 (measured as the S_3 peak). S_1 and S_2 are measured in milligrams of hydrocarbon per gram of sample, and S_3 is milligrams of CO_2 per gram of sample. These units are equivalent to kilograms per metric ton. The temperature at which

maximum S_2 hydrocarbons are produced is known as T_{max}. T_{max} is primarily an indicator of thermal maturity.

Ryder and others (1998) primarily studied Ordovician source rock quality in the Appalachian Basin, but also analyzed 20 Cambrian pre-Knox samples from 3 Rome Trough wells. All of the Rome Trough samples had low total organic carbon (TOC), ranging from 0.08 to 0.84 weight %, with an average of 0.37%, indicating poor to marginal hydrocarbon source potential (Table 7-2). Ryder concluded that Cambrian pre-Knox shales analyzed would have only limited source potential in localized areas, and cannot be considered regional source rocks. Ryder's data is also included on the spreadsheet file on the CD-ROM.

Cole and others (1987) analyzed 46 Cambrian pre-Knox rocks from the subsurface of Ohio. 26 samples of the Conasauga and Kerbel Formations averaged 0.18 weight % TOC, and 20 samples of Mt. Simon Sandstone averaged 0.15%. Complete data is included in Table 7-2 and in the geochemical spreadsheet file on the CD-ROM. Cole and others (1987) considered the Cambrian pre-Knox samples to have marginal to nonsource hydrocarbon potential.

Both of these published studies found very poor hydrocarbon source potential in the pre-Knox samples they analyzed. However, the known hydrocarbon shows and commercial production in the Rome Trough strongly suggest that a Cambrian source exists. The difficulty that previous studies have had in locating rich source rocks indicates there is probably not a widespread regional source, but rather discontinuous, localized organic-rich zones.

New Source Rock Pyrolysis Data

The availability of numerous cores from Cambrian pre-Knox formations presented a unique opportunity to collect additional source rock data in the Rome Trough. There was not funding available in this project for this type of work, but through collaboration with the U.S. Geological Survey, we were able to have 35 samples analyzed using Rock-Eval pyrolysis. We would like to acknowledge this contribution to the project, and thank Bob Ryder, Bob Burruss, and Bob Milici for their help in getting these samples analyzed.

Source rock samples were obtained from cores from 11 pre-Knox wells, primarily from Kentucky and West Virginia. Shales were sampled for analysis, with darker colored shales selected from the cored intervals. There is some bias in the samples, as only intervals cored in the well were sampled. Well cuttings could be used for more complete stratigraphic coverage, but this was beyond the scope of this project. The detailed Rock-Eval data are listed in Table 7-2 and the geochemistry spreadsheet file, and summarized by formation in Table 7-1. A histogram plot of sample frequency vs. TOC by formation is shown in Fig. 7-3. This plot includes only the new data collected in this study, and illustrates the distribution of TOC by formation.

The Rock-Eval data contain some very surprising and encouraging results. Most of the formations sampled had low total organic carbon (TOC) values, commonly less than 1%, with most below 0.5%. These low values are not considered to be capable of generating commercial amounts of hydrocarbons (Peters, 1986). However two wells had samples with significantly higher TOC values (highlighted in bold in Tables 7-1 and 7-2). These samples were from the Rome Formation in the Texaco 1 Kirby well, in Garrard County, Ky., and the Rogersville Shale of the Conasauga Group in the Exxon 1 Smith well, Wayne County, W. Va. These wells are discussed in more detail below.

Texaco Kirby pyrolysis data

Cores of the Rome Formation from the Texaco Kirby well are almost entirely sandstone, but several thin shale beds are present and these were sampled for Rock-Eval analysis. The 4,576 ft sample had low TOC (0.28%), but the sample from 4,628 feet had a TOC of 3.26% (Table 7-2). After this analysis was done, a second sample at 4,628.8 ft (just below the first) was analyzed to determine the extent of the high-TOC shale. The 4,628.8 ft sample was much lower in TOC, with 0.70%. The shale at 4,628 ft is volumetrically small, but does indicate the presence of organic-rich source rocks capable of generating hydrocarbons in the Rome Formation. To characterize the type of organic matter (kerogen) in these samples, hydrogen (HI) and oxygen (OI) indices were calculated from the Rock-Eval data, and plotted on an HI-OI cross plot (Fig. 7-2). While not definitive, the HI-OI plot is useful for initial screening of kerogen types. The plot has several lines that mark the midpoints of the typical spread of data for the various kerogen types. The lines indicate trends of increasing thermal maturity toward the origin (0,0). As Figure 7-2 indicates, the Texaco Kirby samples fall in an area characteristic of both type 1 and 2 kerogen (oil or mixed oil/gas prone) with moderate thermal maturity. In this case, the Rock-Eval data cannot distinguish the exact kerogen type.

Thermal maturity of these rocks can also be determined in several other ways. T_{max}, the temperature during Rock-Eval pyrolysis when maximum hydrocarbons are generated is an indication of the thermal maturity of the source rock. T_{max} values for the Kirby samples were very similar at 444° and 446°C, which indicates the rocks reached the top of the oil window (which ranges from 430 to 470°C). The Rock-Eval data can also be used to calculate the production index (PI), which is S1/(S1+S2). The Kirby samples have PI values of 0.11 and 0.04, which fall just within and below the oil window (PI=0.08–0.5). This is consistent with the T_{max} data.

A third technique for determining thermal maturity is vitrinite reflectance. This involves the systematic change in reflectance of vitrinite, an organic maceral derived from land plants, with increasing temperature. The terrestrial source of vitrinite typically this limits the use of this technique to Silurian and younger rocks (Buchardt and Lewan, 1990). But vitrinite-like macerals have been reported from rocks as old as Cambrian (Buchardt and Lewan, 1990). The origin of this Cambrian vitrinite-like material is not known, but it does exhibit similar changes in reflectance with thermal maturity. Two samples from the Texaco Kirby well were processed to extract kerogen, and examined for vitrinite by Humble Geochemical for the U.S. Geological Survey. Vitrinite-like macerals were

identified in both samples, and reflectance (%R_o) was measured. Mean %R_o for the 2 samples was 0.43 and 0.45 (Fig. 7-11,7-12 and data in spreadsheet file). These values are just below the start of the oil window at 0.50% (Hunt, 1996). However, because these samples are hydrogen-rich, with HI's of 356 and 417, a correction for suppression of vitrinite reflectance in hydrogen-rich kerogen may need to be made (Lo, 1993). R_o values reported here are uncorrected.

Vitrinite reflectance data is also included for three samples from the Texaco 1 Tipton well in Estill Co., Ky. Although these samples have low TOC values, some vitrinite-like material was recovered and analyzed. The samples are deeper than those in the Kirby well, around 6,400 ft. R_o values for this material is slightly higher than the Kirby samples, with mean R_o values of 0.49, 0.51, and 0.53 (Figs. 7-13, 7-14, 7-15).

In summary, the cored interval in the Texaco Kirby core contains thin shales with TOC values high enough to serve as a source of hydrocarbons. The exact type of organic matter cannot be determined from the Rock-Eval data, but it is hydrogen-rich, either oil or oil/gas prone. Thermal maturity is fairly low, just above or at the top of the oil window. Well site core descriptions mention bleeding oil adjacent to the shale bed sampled, possibly indicating that some oil was generated in-situ in this interval. Other intervals in the Kirby well may contain shales with similar geochemical characteristics, but due to the low maturity, oil or gas generation was probably limited in this part of the basin.

Exxon 1 Smith pyrolysis data

The highest quality hydrocarbon source rock in this study was found in the Exxon 1 Smith well, in Wayne Co., W. Va. Nine core samples from the Rogersville Shale of the Conasauga Group and the Rome Formation in the Smith well were analyzed using Rock-Eval pyrolysis. Shales from the Rome Formation in this well were consistently low in TOC (0.13–0.22%), but all 4 samples from the Rogersville Shale contained significant TOC, ranging from 1.20–4.40%. These TOC values fall in the good to very good source potential classification of Peters (1986). Other Rock-Eval data for these samples indicate good hydrocarbon source quality, with higher thermal maturity than the Texaco Kirby samples discussed previously.

The T_{max} values for the Smith samples range from 414-477° C. The single low value of 414° may be anomalous, since heavy free hydrocarbons included in the S_2 peak can result in low T_{max} values (D. Jarvie, Humble Geochemical, personal comm., 2001). Other evidence that heavy hydrocarbons are present in these samples is discussed further below. The other T_{max} values range from 460-477°C, falling in the gas generation window. Assuming a type II, oil and gas prone kerogen, the oil window occurs from T_{max} values of 425–450°C (Espitalie *et al*., 1985, cited in Humble Geochemical Services, unpublished).

An additional indicator of thermal maturity is the production index, PI: $S_1/(S_1+S_2)$. This ratio reflects the conversion of kerogen into free hydrocarbons. PI values for the Smith samples range from 0.51 to 0.58. Values >0.50 fall in the gas window, which is

consistent with the T_{max} and hydrogen index data (discussed below). Vitrinite reflectance data has not been measured for the Smith samples yet. We hope to add this data in the future.

S_1 values for the Smith samples indicate all 4 whole rock samples contain free extractable hydrocarbons. This is verified by the one extracted rock sample, in which all free hydrocarbons were removed by solvents. The S_1 hydrocarbons in the extracted sample are almost negligible, at 0.08. The data table includes a ratio of S1 to TOC (S_1*100/TOC). This ratio is interpreted by Jarvie and Baker (1984) as a show indicator. This ratio for these samples in the range of 50-100, which they indicate as "possible staining, show; mature, tight source rock." These S1 hydrocarbons indicate that oil has been generated in-situ from organic matter in the Rogersville Shale.

S_2 values for the 4 Smith samples indicate the present-day source potential of the rock. These are the hydrocarbons that are generated from cracking of kerogen and high molecular weight hydrocarbons during pyrolysis. S_2 values are lower for the Smith samples than for the Kirby samples. This is most likely a reflection of higher thermal maturity for these samples, with much of the kerogen having already generated hydrocarbons. As noted in the spreadsheet, these samples had a low-temperature shoulder on the S_2 peak during during pyrolysis. This is typically either due to contamination by drilling fluids, or the presence of free heavy natural hydrocarbons that remain behind after the S_1 hydrocarbons are extracted. Since the Smith well was not drilled with oil-based mud, and the samples are from core, contamination can likely be ruled out. The low temperature S_2 peak in these samples is interpreted to come from heavy oil generated in the shale. The extracted rock sample at 11,161.5 ft confirms the presence of hydrocarbons in the sample. The extracted rock analysis shows a lower TOC and S_2, and a much lower S_1, as would be expected from removal of oil in the sample.

The Exxon Smith samples are included in the HI-OI plot in Figure 7-2. Due to their much lower HI values than the Texaco Kirby samples, the Smith samples fall much lower on the HI-OI plot. This is interpreted to reflect the higher thermal maturity of these rocks, which is consistent with their greater depth of burial, higher T_{max} and PI values. The HI-OI plot can sometimes be used to help constrain the type of kerogen in the source rock. The Smith samples likely contain type 1 or type 2 kerogen because of their position on the HI-OI plot. The maturation pathways for types 1 and 2 kerogen merge at lower values of HI, making it impossible to distinguish them on this plot. Type 3 kerogen (woody, terrestrial-sourced kerogen) is not indicated by the HI-OI plot, nor is it geologically reasonable due to the pre-Silurian age (pre-land plants) of the rocks.

OIL AND NATURAL GAS DATA

Published Data

Very few published natural gas analyses from Cambrian reservoirs the Rome Trough were located. Published data was previously compiled by Harris and Baranoski (1996) in the Cambrian pre-Knox play description in the Appalachian Basin gas atlas. We have

also included analyses of Ordovician gases from Central Kentucky in the Trapp and Furnace fields (McGuire and Howell, 1963), one Ordovician gas analysis from the Big Sinking Field, Lee Co., Ky. (B. Miller, pers. comm.), and data from the U.S. Bureau of Mines natural gas database. These published analyses are included in Table 7-3 and in the spreadsheet file. While some of these fields produce from the shallower Ordovician St. Peter Sandstone, the gas composition may have significance to the deeper Cambrian reservoirs in that area.

Gas Quality

The data available from the Rome Trough prior to this study (Table 7-3) show a wide variety in Cambrian gas quality, with total BTU content ranging from 227 to 1175. All of the low-BTU gases are from the western end of the Rome Trough and southwestern Ohio (Garrard and Rockcastle Cos., Ky. and Highland Co., Oh., Fig. 7-1). The low-BTU gases are commonly high in nitrogen, ranging from 27% in Rockcastle Co., Ky. to 80% in Garrard Co., Ky. Carbon dioxide (CO_2) is low in these wells, with a maximum of 1.6% in the Highland County well. Wells farther east in the Trough (Johnson Co., Ky. and Jackson Co., W.Va.) have produced commercial-quality gas. The low-quality gas in the western Rome Trough is also unusual in its higher than normal helium content. Helium ranges from 0.6 to 1.8% in the samples where it was measured. This helium content was significant enough that the U.S. Bureau of Mines included these wells in its inventory of strategic helium reserves. These data are now maintained by the National Technical Information Service run by the U.S. Dept. of Commerce (www.ntis.gov).

An important exploration constraint in the Rome Trough is the extent of low-BTU gas in the basin. Limited drilling and few geochemical analyses of gas shows in the western Rome Trough make it difficult to delineate the boundary of non-commercial gas. High nitrogen gas is known to occur in Cambrian reservoirs in Garrard County, Ky. and Highland County, Ohio. Gas analyses are also available from the Middle Ordovician Sunnybrook (Trenton) and Lower Ordovician Knox in the Hunt's Natural Resources 1 Livesay well (permit 75242), Rockcastle County, Ky. (Table 7-3). Both zones in this well produce gas with 27% nitrogen, 66% methane, negligible CO_2, and 0.6% helium, with a BTU content of around 800. While better quality than the Cambrian reservoirs in nearby Garrard Co., this gas has a significant nitrogen and helium content, and may be derived from a similar source.

Non-commercial gas has also been reported in Estill and Powell Counties, Ky., from the Ordovician St. Peter Sandstone in the Furnace Field (Table 7-3) (McGuire and Howell, 1963). However, the composition of this gas differs from the deeper high nitrogen Cambrian gas. Gas in the Furnace Field contains high CO_2 (26–42%), but low nitrogen (1.4–2.3%). The source of this St. Peter gas is not known, but its composition suggests that it may have a different origin than the Cambrian high-nitrogen gas.

The presence of nitrogen and helium in natural gas can be explained by one of several models. Nitrogen can be derived from atmospheric sources, chemical reactions with red beds, and deep mantle outgassing (Hunt, 1996, p. 230-231). The depth of these nitrogen

reservoirs makes atmospheric contributions unlikely, and the analyses show negligible oxygen, which commonly indicates contamination. Red beds can form nitrogen when iron oxides react with ammonia or nitrogen-bearing organic compounds from thermal alteration of organic matter. While red beds have not been found in significant quantities within the Cambrian sediments in the Rome Trough, there is a thick sequence of Precambrian red beds on the western boundary of the Trough, across the Lexington Fault System. In this area, red sandstones and shales of the Precambrian Middle Run Formation are in fault contact with Cambrian Rome Trough sediments. Thus a red bed origin cannot be ruled out, although there is a limited area along the fault plane for oxidation of ammonia to nitrogen to occur. Middle Run sandstones presently have very low porosity and permeability, so movement of large volumes of ammonia-rich pore fluids through these red beds is unlikely.

Perhaps a more likely model to explain high nitrogen gas is mantle outgassing. The association of nitrogen with higher than average helium is also an indication of a crystalline basement source (Hunt, 1996, p.232). Helium can also be generated by radioactive decay of uranium in sedimentary rocks, but there is no evidence to suggest this has occurred in the Rome Trough. Isotopes of helium (^{3}He and ^{4}He) can be used to determine its source, but there is no isotopic data currently available from these wells. ^{4}He is generated almost entirely by radioactive decay in sedimentary rocks, while ^{3}He is associated with mantle sources. Future isotopic analysis of this helium-rich gas could help to constrain its origin.

Mantle outgassing as a source for the nitrogen and helium gas in the western Rome Trough is geologically reasonable due the proximity to the Grenville Front, a major Precambrian fault. The Grenville Front marks the western edge of the Grenville Province, a metamorphic terrane which was thrust westward over the East Continent Rift Basin (Drahovzal and others, 1992). The Grenville Front is a major thrust fault zone in the Precambrian, and could have provided a pathway for mantle-derived gases to migrate upward into porous Cambrian sandstones. It is worth noting that the Garrard/Rockcastle County area in Kentucky and Highland County in Ohio, where high-helium gases have been reported all lie on or near the Grenville Front (Fig. 7-1).

New Natural Gas and Oil Data

Although not originally a part of the goals of this study, we were able to obtain a number of new gas, condensate, and source rock analyses from ongoing work by the U.S. Geological Survey. The natural gas and condensate analyses were done by the USGS in collaboration with Statoil Energy (now Equitable Resources) from producing wells in the Homer Field, Elliott County, Ky. and an unnamed one-well field in Lawrence County. These data were donated to the Rome Trough Consortium, and should be held confidential to consortium members until published by the USGS. The new source rock data were obtained by the USGS at KGS's request from core material collected during this project. These data should also be held confidential until published by the USGS. Because these data were collected with USGS funds, and were not part of the original consortium work plan, we cannot hold the data confidential with the other project data.

Oil Analyses

In addition to the source rock analyses, Equitable Resources and the USGS provided the consortium with analyses of condensate samples from Homer Field in Elliott County, and from source rock extracts from Garrard County, Ky and Wayne County, W. Va. These data consist of preliminary gas chromatographs of the condensate samples collected from the Elliott County, Ky. gas wells, and 2 extracted samples from the higher TOC source rock in the Texaco 1 Kirby and Exxon 1 Smith wells. The gas chromatographs (GC's) are included as scanned images in this report (Figs. 7-4 through 7-10), and in the geochemistry data file. It is important to note that these are preliminary data, and USGS plans to conduct additional analyses on these samples.

A primary question pertaining to these Cambrian-reservoired hydrocarbons is whether they were sourced from sub-Knox rocks (Cambrian) or younger post-Knox rocks. This distinction is made possible by unique geochemical characteristics of known Ordovician-sourced hydrocarbons. These geochemical characteristics are due the nature of the marine organic matter present during the Ordovician, before the evolution of land plants. While both bacteria and algae contributed to organic matter in Ordovician source rocks, the unique geochemical characteristics are thought to result from an abundance of the microfossil *Gloeocapsomorpha prisca (G. prisca)* (Fowler, 1992). There is debate as to what type of organism *G. prisca* was. Interpretations include a non-photosynthetic, benthic prokaryote that formed mats; a chemosynthetic autotroph, to a phototropic, planktonic, eukaryotic alga (Fowler, 1992). Regardless of its exact affinity, *G. prisca* seems to have been an important organic component in Ordovician and possibly Cambrian sediments.

Much of the published data pertains to Ordovician oils. Data for Cambrian hydrocarbons is more limited, but some researchers feel that the Ordovician characteristics may apply to Cambrian oils and source rocks (Wielens and others, 1990; Fowler, 1992). Oils derived from Ordovician source rocks have distinctive characteristics (Reed and others, 1986; Fowler, 1992; Guthrie and Pratt, 1995):

- a predominance of odd carbon number normal paraffins in the C_{11}–C_{19} range
- low abundance of high molecular weight normal paraffins ($>C_{20+}$)
- very low concentrations of acyclic isoprenoids (pristane and phytane) and polycyclic alkanes
- relatively high concentration of monocyclic alkanes

The most distinctive characteristic of Ordovician oils is the dominance of odd-carbon parraffins from C_9 through C_{19}. The concentration of pristane and phytane varies, but is typically low in Ordovician oils. These compounds are thought to be derived from chlorophyll, and when abundant, suggest a photosynthetic organism was the organic source (Fowler, 1992). A lack of pristane and phytane may indicate that photosynthetic organisms did not contribute to the organic material, and has been noted in oils derived from organic matter rich in *G. prisca*, suggesting that it may have been a non-photosynthetic organism. (Reed and others, 1986; Guthrie and Pratt, 1995).

Since this project has focussed on Cambrian rocks and hydrocarbons, a key question is whether these Ordovician oil characteristics also apply to Cambrian-sourced hydrocarbons. Cambrian oils with characteristics similar to Ordovician oils have been documented by Wielens and others (1990). In addition, alginite similar to *G. prisca* has been identified in rocks as old as Middle Cambrian in the Northwest Territories of Canada (Wielens and others, 1990).

Rome Trough Oils

Eight wells producing from the Cambrian were sampled for gas and condensate. Five preliminary gas chromatographs were run on the condensates by the USGS, and released to the consortium by Equitable Resources. Copies of these GC's are included as Figures 7-4 through 7-8. In addition, GC's were run on extracted hydrocarbons from the higher TOC shales sampled in the Exxon 1 Smith and Texaco 1 Kirby wells by Humble Geochemical (Figs. 7-9, 7-10). The 5 GC's run by USGS on the Elliott County, Ky. oils are preliminary data, and additional analyses are planned by Ryder and Burruss. A more detailed interpretation is necessary before any firm conclusions can be made from these oils.

The Elliott County oils (Figs. 7-4 to 7-8) were collected from stock tanks and gas separators at each well location. Condensate stock tanks were open to the atmosphere, and some of the more volatile components may have been lost due to evaporation. Three of the samples run by USGS were produced from the Cambrian Rome Formation. The other 2 samples are from Ordovician reservoirs in the field, one from the Trenton Limestone, and the other from the St. Peter Sandstone.

Gas chromatographs from the Rome Formation condensates are variable. Two of the three show a predominance of odd carbon normal paraffins in the C_{11} to C_{19} range (Figs. 7-4, 7-5). These samples also have very small abundances of normal paraffins above C_{20} and no significant pristane and phytane peaks. These GC's are similar to published Ordovician-sourced oils, and are likely derived from source rocks as old as Ordovician, and possibly Cambrian. The other Rome sample (Fig. 7-6) differs in that it has no odd carbon normal paraffin dominance, but rather a steep uniform decline in normal paraffins from C_{11} to C_{17}. This sample, from the Carson Associates 1 Pritchard Heirs well, is strongly depleted in the higher weight paraffins. This oil will require further analysis to determine it's origin. Also, the sample from the Carson Associates 40 Kazee well (Fig. 7-4) is slightly contaminated with Tretolite, a chemical used to treat a paraffin problem in this well. The influence of this contaminant is not known in this preliminary analysis.

The two oils produced from Ordovician reservoirs in the field are shown in Figs. 7-7 and 7-8. The Trenton Limestone oil sample from the Carson Associates T-1 Lawson Heirs well (Fig. 7-7) has the typical Ordovician odd carbon number dominance in the C_{11}-C_{19} range, but differs slightly in the small, but observable phristane and phytane peaks. This oil is much darker in color than the deeper Rome oils, but whether this is due to a different source is not known. The condensate sample from the St. Peter Sandstone reservoir in the field is shown in Fig. 7-8. This sample shows a sharp decline in the

heavier normal alkanes (C_{14}-C_{20}), and does not show an odd carbon-dominance in the C11-C20 range. A full interpretation of this sample will have to wait until more work is done by USGS.

Finally, gas chromatographs were run on 2 extracted oils from potential source rocks in the Exxon 1 Smith and Texaco 1 Kirby wells discussed previously (Figs. 7-9, 7-10). These chromatographs were interpreted by Dan Jarvie of Humble Geochemical in Houston, Texas. His interpretation follows below:

"We extracted the two samples from the Exxon Smith and Texaco Kirby wells and ran GC fingerprints (Figs. 7-9 and 7-10). They are very similar in that they both have n-C_{17} and n-C_{19} predominance with odd predominance from C_{11}-C_{19} and are composed primarily of normal alkanes. You will note that the isoprenoid content, e.g., what we think are pristane and phytane, is very low; this is also typical of the Ordovician oils. The C_{17} and C_{19} predominance is seen in Ordovician oils derived from *G. prisca* sources. However, these oils are a bit more waxy than typical Ordovician oils having relatively high abundance of alkanes extending into the C_{30} range. Ordovician oils usually die around C_{20}, although some Ordovician oils do have a slightly more waxy fingerprint. The Kirby extract is slightly different from the Smith extract in that it is more waxy and has slight C_{21} predominance. It also contains more light hydrocarbons but this could be a sample preparation artifact. Please note that all peak identification are tentative based on retention times and being a homologous series. While I have compared these to Ordovician oils, this is by no means conclusive as I would expect Cambro-Ordovician oils to be somewhat similar based on the limited biomass available to generate these oils. Thus, I certainly would not attempt to rule out a Cambrian source either. These oils are somewhat similar to the White Pines Precambrian oil recovered from a copper mine seep in Wisconsin (mostly n-alkanes, limited compositional variation) and even the Cambrian Deadwood oil, although it contains abundant pristane and phytane. All these oils look virtually like a saturate fraction GC even though these are whole extract fingerprints.

The extracted rock from the Smith well contains lower S_1 and S_2 after extraction as I suspected based on the presence of a low temperature S_2 shoulder in the whole rock pyrogram."

Thus based on the preliminary analyses done to date, extracted hydrocarbons from Cambrian source rocks in 2 wells match the GC fingerprint of produced condensate from the Homer Field in Elliott Co., Ky. This correlation will be refined with additional work by the USGS.

Rome Trough Gas Analyses

Natural gas and condensate were sampled from 8 Cambrian sub-Knox producing wells. Seven of these wells are within the Homer Field in Elliott County, Ky. The other well (Carson Associates 1 Ray) produces from a separate structure in Lawrence Co., Ky. Gas was sampled at the separator, and condensate samples were obtained either from the separator or from stock tanks. All of the wells were flowing gas when sampled, with the

exception of the Carson Associates 18 Blair well in the Homer Field. This well produces from the Ordovician St. Peter Sandstone, and was temporarily shut-in. This well and other St. Peter Sandstone producers in the area have reported small concentrations of H_2S (5-30 ppm, M. Hay, personal comm., 2001), but H_2S was not included in the analyses done by the USGS. There have been no reports of H_2S from Cambrian zones in the Homer Field.

Composition and isotope data from 8 gas samples are included in the spreadsheet, and are summarized in Table 7-4. The analyses were done by Isotech Laboratories, Inc., Champaign, Il. The Cambrian gas contains varying amounts of condensate, and most of the gas can be classified as wet (> 0.3 gallons of liquids per MCF). Production data obtained in the field for one of the higher producing wells, the Eastern States 34 Kazee, indicated a daily rate of 1,248 MCFG with 29 bbl. condensate.

All of the Cambrian gas sampled is of commercial quality, with an average BTU content of 1098 (Table 7-4). Methane averages 87%, and nitrogen and CO_2 are low, averaging 3.5% and 0.09% respectively. These gases differ significantly from those in the western Rome Trough discussed previously. This could be explained by their distance from the Grenville Front (assuming that is the source of the high nitrogen gas). The producing area is also deeper and more thermally mature, lying closer to the deepest parts of the Rome Trough. This might also explain why this area has commercial quality gas, while the western Rome Trough does not.

The USGS data also includes carbon isotopic analyses for various gas constituents. These data are included in the spreadsheet, but have not been interpreted by us.

SUMMARY AND CONCLUSIONS

The geochemistry part of this study has resulted in several important new findings. First, potential hydrocarbon source rocks of Cambrian age have been documented for the first time in the Appalachian Basin. The extent of these source rocks is widespread, but the distribution is not likely to be uniform. High TOC shales were found in Garrard County, Ky. and Wayne County, W. Va. in the Rome Formation and Conasauga Group (Rogersville Shale). The volume of these organic-rich shales in the Rome Trough is not currently known. The Garrard County shales are thin and volumetrically small. The Rogersville Shale interval in the Exxon 1 Smith well in Wayne County, W. Va. is thick enough to map based on geophysical log characteristics. Future work should attempt to determine the extent of this source interval.

Analysis of Cambrian oils (condensates) from wells in Elliott County, Ky. shows characteristics of Ordovician or older sources. These characteristics include a predominance of odd-carbon normal alkanes in the C11–C20 range, low abundance of high molecular weight normal paraffins ($>C_{20+}$), and low abundance of pristane and phytane. Additional work needs to be done on these oils by the USGS, but the preliminary data matches known Ordovician and older oils fairly well. The oils also match gas chromatograms run on hydrocarbons extracted from the high TOC source

rocks in Garrard Co., Ky. and Wayne Co., W. Va. This match indicates that the Elliott County hydrocarbons could have been sourced from Cambrian shales within the Rome Trough.

Cambrian natural gas quality varies significantly across the study area, with low-BTU, high nitrogen gas encountered in the western part of the study area (Garrard and Rockcastle Counties, Ky. and Highland County, Ohio). . High-BTU, commercial quality Cambrian gas occurs in Elliott, Lawrence, and Johnson Counties, Ky, and in Jackson Co., W. Va. The exact boundary for non-commercial gas in the Rome Trough is not well-constrained, but exploration risk probably increases west of Estill Counties, Ky. where gas high in CO_2 occurs in Ordovician reservoirs. It is not known if the Cambrian high-nitrogen gas is related to the Ordovician high-CO_2 gas. Risk of high nitrogen in Cambrian reservoirs increases with proximity to the Grenville Front, a Precambrian fault zone. A correlation of high nitrogen in Cambrian wells near the Grenville Front has been observed in Kentucky and Ohio, suggesting a deep basement source of nitrogen (and associated anomalous helium in these wells). Commerical-quality gas is produced from the Knox and overlying Ordovician High Bridge/Lexington carbonates (Black River/Trenton equivalents) in Clay County, Ky. along the Rockcastle River uplift.

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REFERENCES

Buchardt, B., and Lewan, M.D., 1990, Reflectance of vitrinite-like macerals as a thermal maturity index for Cambrian-Ordovician Alum Shale, southern Scandinavia: AAPG Bull., v. 74, p. 394-406.

Cole, G.A., Drozd, R.J., Sedivy, R.A., and Halpern, H.I., 1987, Organic geochemistry and oil-source correlations, Paleozoic of Ohio: AAPG Bull., v. 71, p. 788-809.

Drahovzal, J. A., Harris, D. C., Wickstrom L. H., Walker, Dan, Baranoski, M. T., Keith, Brian, and Furer, L. C., 1992, The East Continent Rift Basin: a new discovery: Kentucky Geological Survey, Special Publication 18, Series XI, 25 p.

Elmore, R.D., and Daniels, P.A., 1988, The Nonesuch Formation: lacustrine sedimentation in a Precambrian Mid-Continent rift basin: in Daniels, P.A., Jr. and

D. Elmore (eds.), Upper Keeweenawan rift-fill sequence, Mid-Continent Rift System, Michigan, Michigan Basin Geological Society, 1988 Fall Field Trip Guidebook, p. 103-125.

Espitalie, J., Deroo, G., and Marquis, F., 1985, Rock-Eval Pyrolysis and its Applications, Institut Francais du Petrole Geologie No. 27299, Project B41 79008.

Fowler, M.G., 1992, The influence of *Gloeocapsomorpha prisca* on the organic geochemistry of oils and organic-rich rocks of Late Ordovician age from Canada: in M. Schidlowski et al. (eds.), Early Organic Evolution: Implications for Mineral and Energy Resources, Springer-Verlag, Berlin Heidelberg, p. 336-356.

Guthrie, J.M. and Pratt, L.M., 1995, Geochemical character and origin of oils in Ordovician reservoir rock, Illinois and Indiana, USA: AAPG Bull., v. 79, p. 1631-1649.

Harris, D.C. and Baranoski, M.T., 1996, Play Cpk: Cambrian Pre-Knox Group Play: *in* Roen, J.B. and Walker, B.J. (eds.), The Atlas of Major Appalachian Gas Plays, W. Va. Geological and Economic Survey Publication V-25, p. 188-192.

Hunt, John M., 1996, Petroleum Geochemistry and Geology: W.H. Freeman, New York, second edition, 743 p.

Jarvie, D.M., and Baker, D.R., 1984, Application of the Rock-Eval III oil show analyzer to the study of gaseous hydrocarbons in an Oklahoma gas well, 187th ACS National Meeting, St. Louis.

Lo, H.B., Correction for the suppression of vitrinite reflectance in hydrogen-rich kerogens; preliminary guidelines: Organic Geochemistry, v. 20, p. 653-657.

Longman, M.W. and Palmer, S.E., 1987, Organic geochemistry of Mid-Continent Middle and Late Ordovician Oils: AAPG Bull., v. 71, p. 938-950.

McGuire, W. H., and Howell, P., 1963, Oil and gas possibilities of the Cambrian and Lower Ordovician in Kentucky: Lexington, Kentucky, Spindletop Research Center, 216 p.

Obermajer, M.G., Fowler, M.G., and Snowdon, L.R., 1999, Black shale source rocks and oil generation in the Cambrian and Ordovician of the Central Appalachian Basin, USA: Discussion: AAPG Bull., v. 83, p. 807-810.

Peters, K.E., 1986, Guidelines for evaluating petroleum source rocks using programmed pyrolysis: AAPG Bull., v. 70, p. 318-329.

Reed, J.D., Illich, H.A., and Horsfield, B., 1985, Biochemical evolutionary significance of Ordovician oils and their sources: Organic Geochemistry, v. 10, p. 347-358.

Ryder, R.T., Burruss, R.C., and Hatch, J.R., 1991, Geochemistry of selected oil and source rock samples from Cambrian and Ordovician strata, Ohio-West Virginia-Tennessee, part of the Appalachian basin: U.S. Geological Survey Open-File Report 91-434, 71 p.

Ryder, R.T., Burruss, R.C., and Hatch, J.R., 1998, Black shale source rocks and oil generation in the Cambrian and Ordovician of the central Appalachian Basin, USA: AAPG Bull., v. 82, p. 412-441.

Tissot, B.P. and Welte, D.H., 1978, Petroleum Formation and Occurrence: Springer-Verlag, New York, 538 p.

Webb, E.J., 1980, Cambrian sedimentation and structural evolution of the Rome trough in Kentucky: Ph.D. Thesis, University of Cincinnati, 107 p.

Wielens, J.B.W., von der Dick, H., Fowler, M.G., Brooks, P.W., and Monnier, F., 1990, Geochemical comparison of a Cambrian alginite potential source rock, and hydrocarbons from the Colville/Tweed Lake area, Northwest Territories: Bull. Of Canadian Pet. Geology, v. 38, p. 236-245.

Table 7-1: Summary of Rock-Eval data for Cambrian rocks in the study area. Numbers in bold print indicate samples with higher TOC values. New data in this study was contributed by the USGS.

Study	Formation	Number of samples	Total Organic Carbon (%)			S_2 Yield (kg/ton)		
			Ave.	High	Low	Ave.	High	Low
Cole et al. 1987	Conasauga/ Kerbel	26	0.18	0.67	0.00	0.19	2.03	0.00
Cole et al. 1987	Mt. Simon Ss.	20	0.15	0.45	0.00	0.11	0.65	0.00
Ryder et al. 1998	Conasauga/ Rome	20	0.37	0.84	0.08	0.14	0.41	0.00
This study (USGS)	Nolichucky Shale	9	0.12	0.15	0.10	0.12	0.22	0.01
This study (USGS)	Maryville Limestone	4	0.61	1.12	0.24	0.31	0.65	0.12
This study (USGS)	Rogersville Shale	**5**	**2.73**	**4.40**	**1.20**	**1.49**	**2.58**	**0.75**
This study (USGS)	Rome Fm.	17	0.40	**3.26**	0.08	1.02	**13.61**	0.01

Table 7-2: Detailed Rome Trough Rock-Eval pyrolysis data. Numbers in bold indicate samples with higher TOC. Table continued on next page. New data was contributed to this study by the USGS.

API No.	Well	Location	Formation	Depth	TOC	T_{max}	HI	OI	S1	S2	S3	S1*100 /TOC	S2/S3	PI	Source
n/a	average of 26 samples	Ohio	Conasauga Gp and Kerbel Fm.	N/a	ave=0.18	n/a	n/a	n/a	n/a	ave=0.19	n/a	n/a	n/a	n/a	Cole et al., 1987
n/a	average of 20 samples	Ohio	Mt. Simon Ss	N/a	ave=0.15	n/a	n/a	n/a	n/a	ave=0.11	n/a	n/a	n/a	n/a	
4710700351	Hope Nat. Gas 9634 Power Oil	Wood Co., WV	Rome Fm	13,128.0	0.18		246	155	0.31	0.39	0.28	172	1.39	0.44	Ryder et al. 1998
4710700351	Hope Nat.Gas 9634 Power Oil	Wood Co., WV	Rome Fm	13,133.0	0.18		0	127	0	0	0.23	0		0.00	
4710700351	Hope Nat. Gas 9634 Power Oil	Wood Co., WV	Rome Fm	13,139.8	0.08		12	337	0	0.01	0.27	0	0.04	0.00	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	13,985.5	0.34		20	97	0.03	0.07	0.33	9	0.02	0.30	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	14,136.0	0.36		19	88	0.04	0.07	0.32	11	0.02	0.40	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	14,364.5	0.19		26	200	0.02	0.05	0.38	11	0.02	0.33	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	14,380.5	0.59		18	54	0.13	0.11	0.32	22	0.04	0.54	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	14,386.5	0.25		40	112	0.09	0.1	0.28	36	0.03	0.50	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Maryville Ls	14,400.5	0.51		29	86	0.12	0.15	0.44	24	0.07	0.46	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rogersville Sh	14,660.0	0.57	425	33		0.11	0.19		19		0.37	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rogersville Sh	15,530.0	0.53	392	68		0.49	0.36		92		0.57	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rogersville Sh	15,532.0	0.29		48	86	0.13	0.08	0.25	45	0.02	0.50	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rutledge Ls	15,560.5	0.33		15	115	0.03	0.07	0.38	9	0.03	0.37	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Pumpkin Valley Sh and Rome Fm	15,830.0	0.74	426	41		0.19	0.3		26		0.38	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rome Fm	16,310.0	0.84	428	49		0.23	0.41		27		0.36	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rome Fm	16,461.0	0.09		88	177	0.05	0.08	0.16	56	0.01	0.42	
4703501366	Exxon 1 McCoy et.al.	Jackson Co., WV	Rome Fm	16,493.0	0.11		63	190	0.05	0.07	0.21	45	0.01	0.42	
4705900805	Columbia Gas 9674T Mineral Tract 10	Mingo Co, WV	Rome Fm	16,233.5	0.15		33	180	0.04	0.05	0.27	27	0.01	0.50	
4705900805	Columbia Gas 9674T Mineral Tract 10	Mingo Co, WV	Rome Fm	16,235.5	0.51		15	54	0.12	0.08	0.28	24	0.02	0.60	
4705900805	Columbia Gas 9674T Mineral Tract 10	Mingo Co, WV	Rome Fm	16,239.5	0.58		15	46	0.15	0.09	0.27	26	0.02	0.62	
1611567549	Ashland 1 Williams	Johnson Co., KY	Nolichucky Sh	6,270.6	0.12	494	158	258	0.06	0.19	0.31	50	0.61	0.24	USGS/ RTC (This study)
1611567549	Ashland 1 Williams	Johnson Co., KY	Nolichucky Sh	6,275.0	0.13	421	69	146	0.05	0.09	0.19	38	0.47	0.36	
1611567549	Ashland 1 Williams	Johnson Co., KY	Nolichucky Sh	6,280.0	0.15	444	147	187	0.04	0.22	0.28	27	0.79	0.15	
1611567549	Ashland 1 Williams	Johnson Co., KY	Nolichucky Sh	6,285.5	0.1	506	470	230	0.03	0.17	0.23	30	0.74	0.15	
1611567549	Ashland 1 Williams	Johnson Co., KY	Nolichucky Sh	6,292.0	0.12	500	83	125	0.04	0.1	0.15	33	0.67	0.29	
1607921048	Texaco 1 Kirby	Garrard Co, KY	Maryville Ls (equiv.)	4,576.0	0.28	438	232	107	0.05	0.65	0.3	18	2.17	0.07	

API No.	Well	Location	Formation	Depth	TOC	T_{max}	HI	OI	S1	S2	S3	S1*100 /TOC	S2/S3	PI	Source
1607921048	Texaco 1 Kirby	Garrard Co, KY	Rome Fm	4,628.0	**3.26**	**444**	**417**	**11**	**0.55**	**13.61**	0.35	17	38.89	0.04	
1607921048	Texaco 1 Kirby	Garrard Co, KY	Rome Fm	4,628.8	**0.70**	**446**	**356**	**16**	**0.30**	**2.49**	0.11	43	22.64	0.11	USGS/ RTC (This study)
1606521865	Texaco 1 Tipton	Estill Co, Ky	Rome Fm	6,375.5	0.17	448	53	76	0.01	0.09	0.13	6	0.69	0.10	
1606521865	Texaco 1 Tipton	Estill Co, Ky	Rome Fm	6,385.0	0.16	450	31	19	0	0.05	0.03	0	1.67	0.00	
1606521865	Texaco 1 Tipton	Estill Co, Ky	Rome Fm	6,389.5	0.12	447	75	17	0	0.09	0.02	0	4.50	0.00	
4703501366	Exxon 1 McCoy	Jackson Co., WV	Black River Gp	9,294.8	0.88	392	16	28	0.24	0.14	0.25	27	0.56	0.63	
4704301469	Exxon 1 McCormick	Lincoln Co., WV	Maryville Ls	13,650.0	0.79	400	15	8	0.15	0.12	0.06	19	2.00	0.56	
4704301469	Exxon 1 McCormick	Lincoln Co., WV	Maryville Ls	13,661.0	1.12	348	20	10	0.23	0.22	0.11	21	2.00	0.51	
4704301469	Exxon 1 McCormick	Lincoln Co., WV	Rome Fm	16,255.0	0.83	299	8	18	0.15	0.07	0.15	18	0.47	0.68	
4704301469	Exxon 1 McCormick	Lincoln Co., WV	Rome Fm	16,906.0	0.13	392	46	46	0.1	0.06	0.06	77	1.00	0.63	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rogersville Sh	11,150.5	**2.83**	**460**	**61**	**13**	**1.79**	**1.72**	0.36	63	4.78	0.51	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rogersville Sh	11,161.5	**4.40**	**469**	**59**	**6**	**2.71**	**2.58**	0.27	62	9.56	0.51	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rogersville Sh	11161.5 (extract)	**3.16**	**477**	**40**	**10**	**0.08**	**1.26**	0.32	3	3.94	0.06	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rogersville Sh	11,180.5	**1.20**	**414**	**63**	**23**	**0.81**	**0.75**	0.27	68	2.78	0.52	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rogersville Sh	11,195.5	**2.08**	**465**	**55**	**12**	**1.60**	**1.15**	0.25	77	4.60	0.58	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rome Fm	12,440.3	0.15	475	13	100	0.03	0.02	0.15	20	0.13	0.60	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rome Fm	12,478.5	0.22	361	32	50	0.03	0.07	0.11	14	0.64	0.30	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rome Fm	12,497.0	0.14	299	7	50	0.03	0.01	0.07	21	0.14	0.75	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rome Fm	13,710.5	0.13	319	38	85	0.03	0.05	0.11	23	0.45	0.38	
4709901572	Exxon 1 Smith	Wayne Co., WV	Rome Fm	13,734.5	0.21	299	43	48	0.04	0.09	0.10	19	0.90	0.31	
1604534578	Cities Service 1 Garrett	Casey Co., KY	Rome Fm	7,242.0	0.18	423	33	28	0.03	0.06	0.05	17	1.20	0.33	
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Rome Fm	6,814.5	0.12	449	142	50	0.03	0.17	0.06	25	2.83	0.15	
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Rome Fm	6,828.0	0.15	435	127	67	0.05	0.19	0.10	33	1.90	0.21	
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Rome Fm	6,835.0	0.13	477	154	54	0.04	0.20	0.07	31	2.86	0.17	
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Nolichucky Sh	5700-5800	0.15	420	127	160	0.07	0.19	0.24	47	0.79	0.27	
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Maryville Ls	5970-6000	0.24	431	104	75	0.16	0.25	0.18	67	1.39	0.39	
1615121905	Texaco 1 Perkins	Madison Co., KY	Rome Fm	4,770.0	0.08	450	25	125	0.02	0.02	0.10	25	0.20	0.50	
1623730520	Exxon 1 Banks	Wolfe Co., KY	Nolichucky Sh	7,341.5	0.10	338	10	80	0.03	0.01	0.08	30	0.13	0.75	
1623730520	Exxon 1 Banks	Wolfe Co., KY	Nolichucky Sh	7,377.0	0.10	299	50	120	0.02	0.05	0.12	20	0.42	0.29	
3414560141	Aristech Chemical 4 Monitor Well	Scioto Co., OH	Nolichucky Sh	5,137.8	0.12	299	50	92	0.03	0.06	0.11	25	0.55	0.33	

Table 7-3: Published and contributed natural gas analyses from Ordovician and Cambrian reservoirs in the study area.

API No.	Well	Location	Producing Zone	BTU	He	N	CO_2	Methane	Ethane	Propane	Iso-butane	N-bu-tane	Iso-pen-tane	N-pen-tane	H_2S	Source
1604905543	Smith 1 Chambers	Clark Co., KY	Ord. St. Peter Sandstone	955	nd	5.96	2.96	88.25	1.66	0.19	0.20	0.27	0.17	0.18	0.15	McGuire and Howell, 1963
1604908246	Melcher 1 Shephard	Clark Co., KY	Ord. St. Peter Sandstone	952	nd	5.76	3.18	88.36	1.62	0.37	0.14	0.15	0.06	0.07	0.15	
1604908448	Melcher 1 Barrett	Clark Co., KY	Ord. St. Peter Sandstone	953	nd	6.07	2.67	88.74	1.71	0.30	0.13	0.13	0.12	0.1	0.00	
1606500489	Petroleum Exploration 1 McIntosh	Estill Co., KY	Ord. St. Peter Sandstone	758	nd	1.44	25.54	69.93	1.79	0.70	0.10	0.25	0.09	0.07	nil	
1606500490	Petroleum Exploration 1 Newkirk	Estill Co., KY	Ord. St. Peter Sandstone	646	nd	2.04	37.6	57.88	1.14	0.42	0.07	0.14	0.12	0.13	nil	
1606500492	South Central Petroleum 3 Garrett	Estill Co., KY	Ord. St. Peter Sandstone	764	nd	nd	18.2	67.45	nd	nd	nd	nd	nd	nd	nil	
1606500492	South Central Petroleum 3 Garrett	Estill Co., KY	Ord. St. Peter Sandstone	643	nd	nd	34.9	59.05	nd	nd	nd	nd	nd	nd	nil	
1606500492	South Central Petroleum 3 Garrett	Estill Co., KY	Ord. St. Peter Sandstone	572	nd	nd	40.9	54.00	nd	nd	nd	nd	nd	nd	0.5	
1606500492	South Central Petroleum 3 Garrett	Estill Co., KY	Ord. St. Peter Sandstone	566	nd	nd	41.95	53.04	nd	nd	nd	nd	nd	nd	0.55	
1619700491	Carpenter 1 Wise	Powell Co. KY	Ord. St. Peter Sandstone	n/a	nd	2.28	41.04	54.68	0.95	0.23	0.04	0.10	0.04	0.01	0.56	
1607921048	Texaco 1 Kirby	Garrard Co, KY	Camb. Rome Formation	227	1.62	80.4	0.01	13.90	2.1	0.60	0.00	0.30	0	0.2	nd	Harris and Baranoski, 1996
1607921048	Texaco 1 Kirby	Garrard Co, KY	Camb. Rome Formation	240	1.81	79.3	<.05	14.50	2.2	0.60	0.00	0.30	0	0.4	nd	
1607925811	Widener 1 Burdette	Garrard Co, KY	Camb. Rome Formation	339	1.8	70.7	0	19.30	4.5	0.70	0.50	0.70	0.1	0.2	nd	
1611567549	Ashland No.1 Williams	Johnson Co, KY	Camb. Nolichucky Sh	1175	nd	2		81.00	9	4.00	<1	1		<1	nd	
3407120016	Oxford Heyob-Coyne-West Unit	Highland Co, OH	Camb. Eau Claire Fm	723	nd	32.64	1.63	60.23	3.14	1.43	0.14	0.46	0.06	0.15	nd	
4703501366	Exxon No.1 McCoy	Jackson Co, WV	Camb. Conasauga Gp	1022	nd	1		97.00	2	<1	<.01	<.01		<.01	nd	
1612960010	Ashland 1 Cable, Millard	Lee Co., KY	Ord. Beekmantown/ Rose Run Ss	869	nd	4.86	14.42	75.00	3.52	1.34	0.13	0.37	0.08	0.07	nd	Bretagne GP.
1620375242	Hunt's Natural Resources 1 Livesay	Rockcastle Co., KY	Ord. Trenton Limestone	801	0.6	27	<0.05	66.60	3.8	1.20	0.40	0.20	0.1	0	nd	NTIS Database
1620375242	Hunt's Natural Resources 1 Livesay	Rockcastle Co., KY	Ord. Knox Group	796	0.6	27.7	0.1	65.60	3.9	1.20	0.30	0.30	0.2	0	nd	

Table 7-4: New natural gas analyses from Cambrian reservoirs in the Homer Field in Elliott Co., Ky. and an unnamed field in Lawrence Co., Ky. Data was contributed by the USGS and Equitable Resources, and is confidential to the Rome Trough Consortium.

API No.	Well	Location	Produc-ing Fm.	BTU	Me-thane	Etha ne	Pro-pane	N-Bu-tane	Iso-Bu-tane	N-Pen-tane	Iso-Pen-tane	Hex-anes+	N	CO_2	H	Ar	He
1612789172	Carson Associates 1 Ray	Lawrence Co., KY	Camb. Cona-sauga	1066	92.84	3.31	1.09	0.34	0.18	0.13	0.12	0.23	1.38	0.31	0.005	0.0094	0.053
1606388019	Carson Associates 57 Prichard Heirs	Elliott Co., KY	Camb. Rome Fm	1087	89.95	4.05	1.64	0.61	0.19	0.25	0.14	0.41	2.62	0.01	0.028	0.018	0.081
1606390473	Eastern States 39 Fannin	Elliott Co., KY	Camb. Rome Fm	1150	82.71	7.33	3.6	1.21	0.044	0.33	0.25	0.25	3.76	0.01	0.0091	0.021	0.072
1606389000	Carson Associates 40 Kazee	Elliott Co., KY	Camb. Rome Fm	1087	92.13	3.63	1.23	0.47	0.19	0.2	0.15	0.43	1.41	0.07	0.031	0.011	0.053
1606387821	Carson Associates T-1 Lawson Heirs	Elliott Co., KY	Ord. Trenton Ls	1125	81.64	7.81	3.54	0.92	0.35	0.2	0.17	0.23	4.75	0.06	0.19	0.013	0.13
1606388355	Carson Associates 18 Blair	Elliott Co., KY	Ord. St. Peter Ss.	1037	90.98	3.29	0.97	0.29	0.12	0.1	0.078	0.21	3.58	0.17	0.06	0.032	0.1
1606390472	Eastern States 34 Kazee	Elliott Co., KY	Camb. Cona-sauga/ Rome	1114	83.13	6.86	2.74	0.9	0.34	0.33	0.24	0.32	5	0.01	0.011	0.025	0.094
1606387820	Carson Associates 33 Lawson	Elliott Co., KY	Camb. Rome Fm	1120	81.83	6.61	2.9	1.02	0.35	0.43	0.29	0.53	5.85	0.04	0.0065	0.041	0.1
			Average	**1098**	**86.90%**	**5.36%**	**2.21%**	**0.72%**	**0.22%**	**0.25%**	**0.18%**	**0.33%**	**3.54%**	**0.09%**	**0.04%**	**0.02%**	**0.09%**

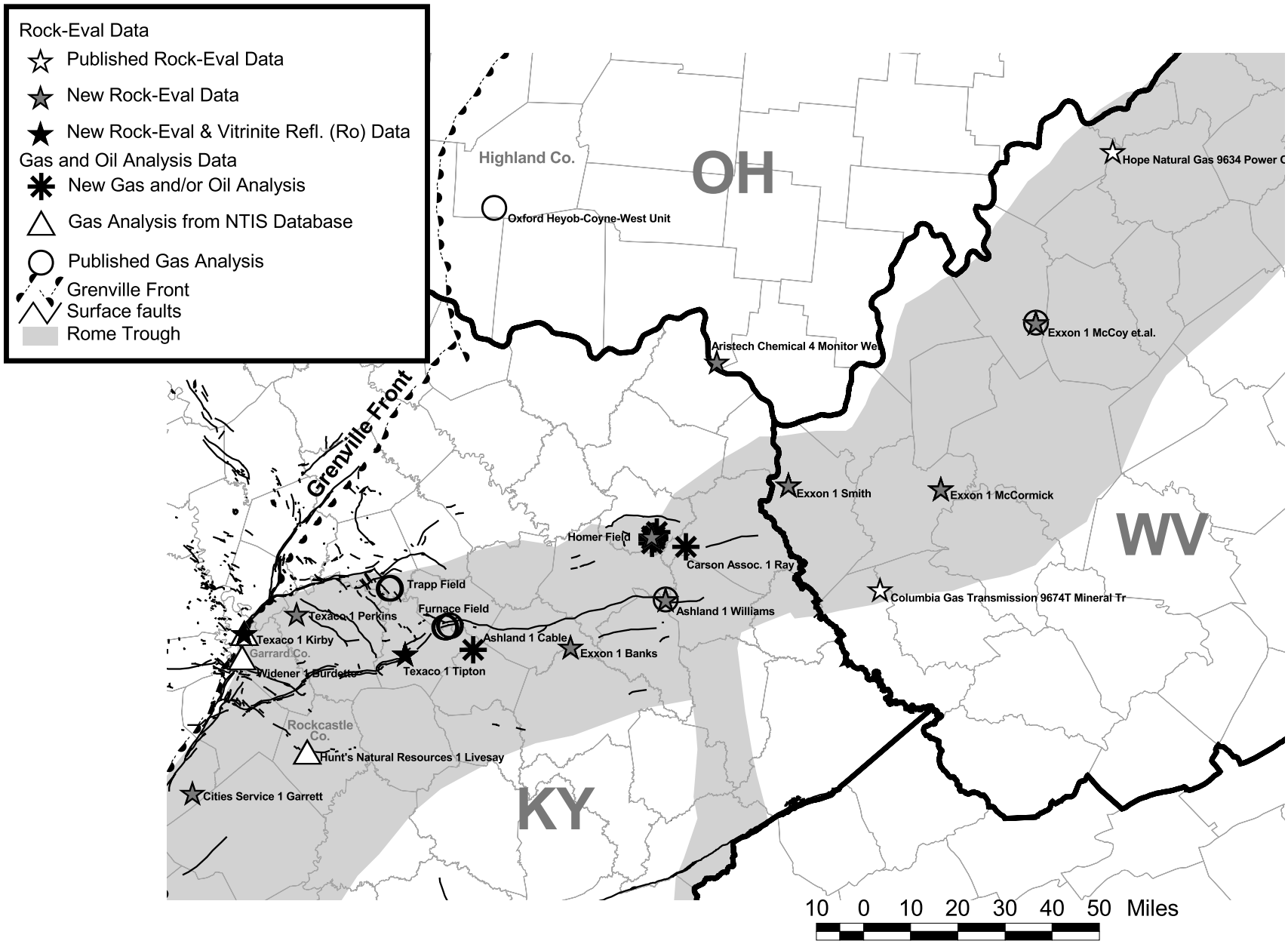


Figure 7-1. Map of Rome Trough study area showing distribution of new and previously published geochemical and thermal maturity data.

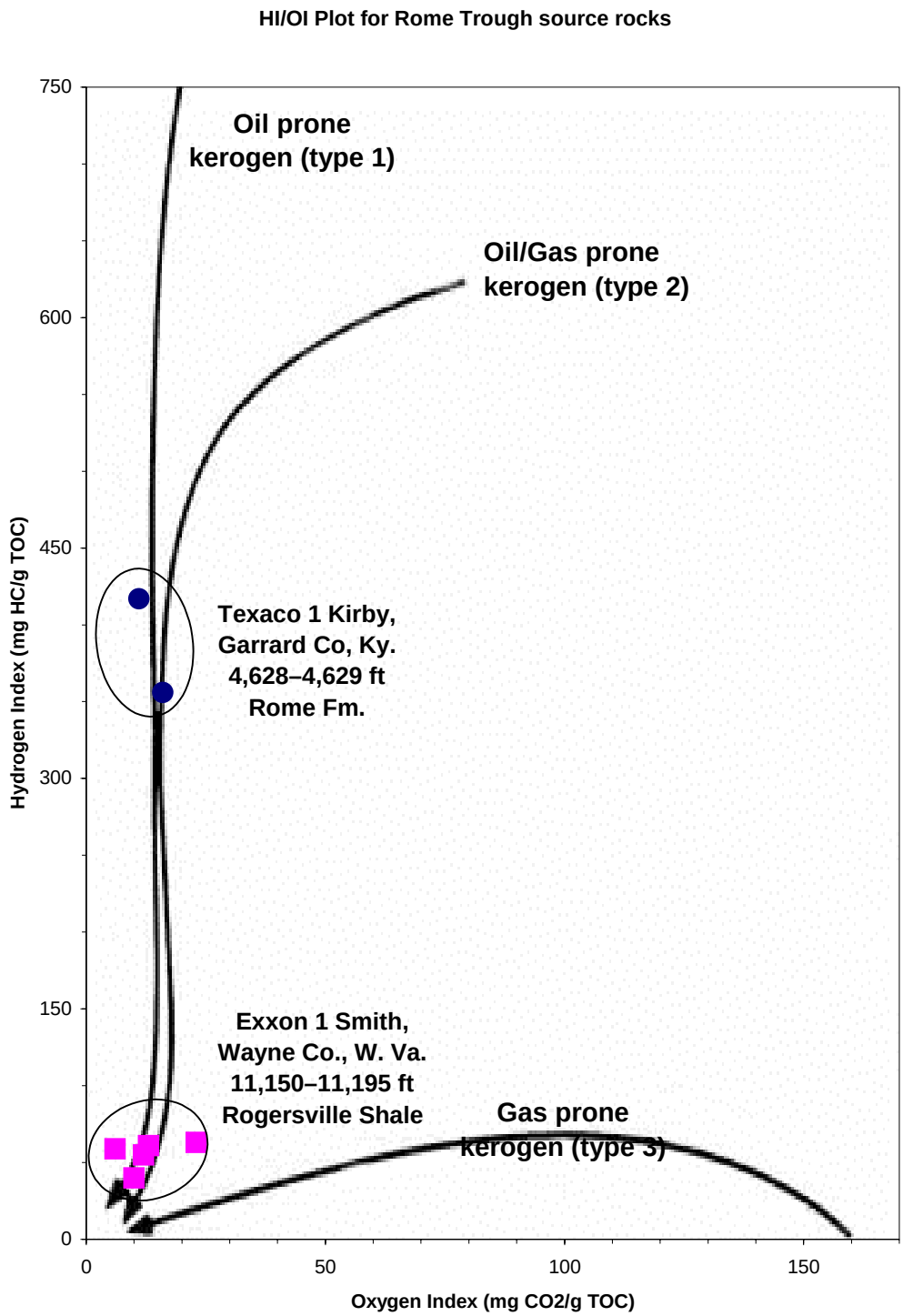


Figure 7-2. Plot of hydrogen index vs. oxygen index for samples with significant total organic carbon content. Thermal maturity of the kerogen increases from upper right to lower left. Samples from Garrard Co., Ky. are less thermally mature and plot higher on the hydrogen axis than the deeper samples from Wayne Co., W. Va. This type of plot is sometimes useful for determining the type of kerogen present, but is not diagnostic for these samples.

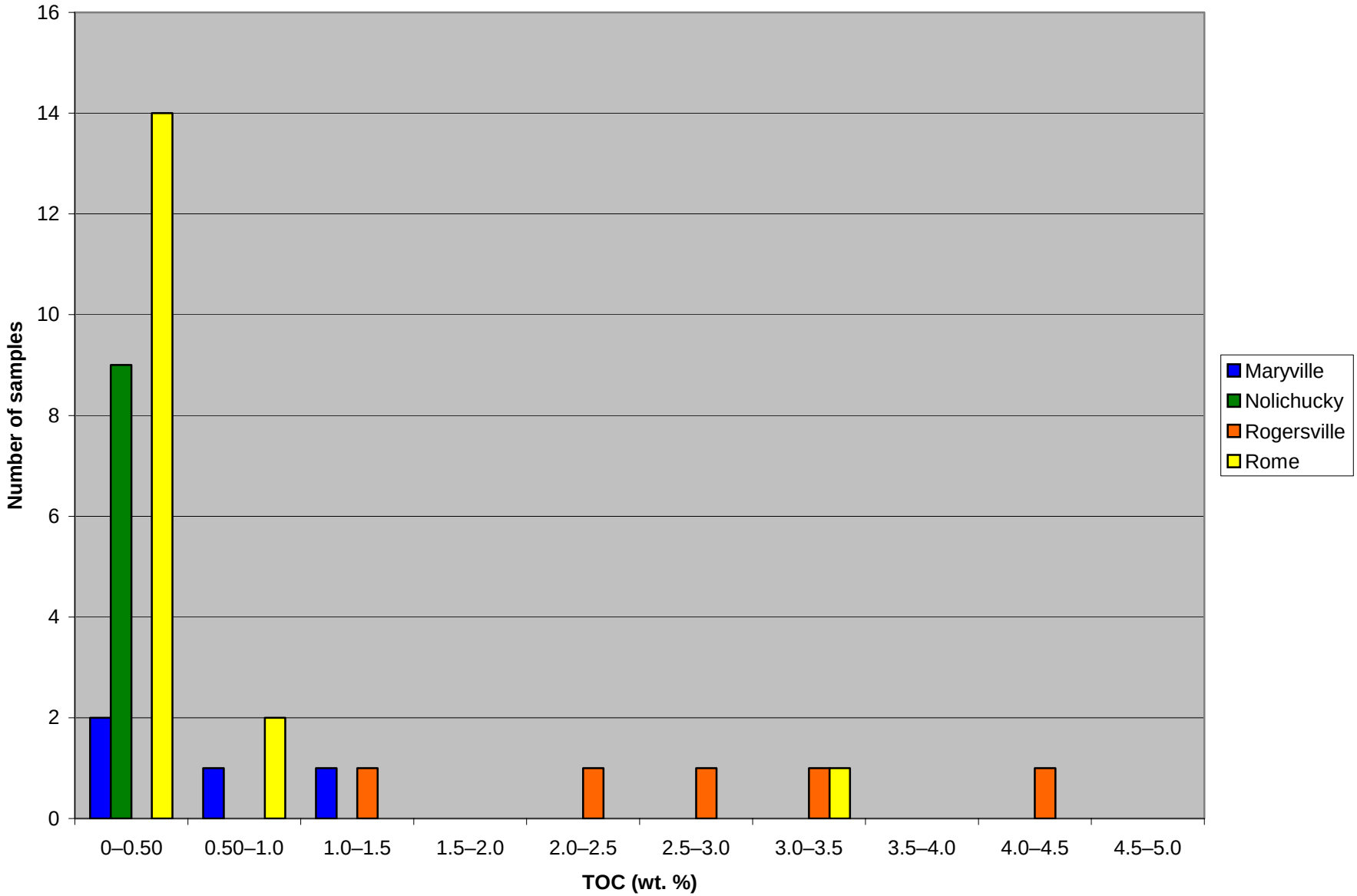


Fig. 7-3. Histogram showing range of total organic carbon (TOC) for Rome and Conasauga core samples analyzed in this study (n=35). The majority of samples are lean to very lean in TOC, but potential source rocks were identified in the Rogersville Shale and Rome Formation.

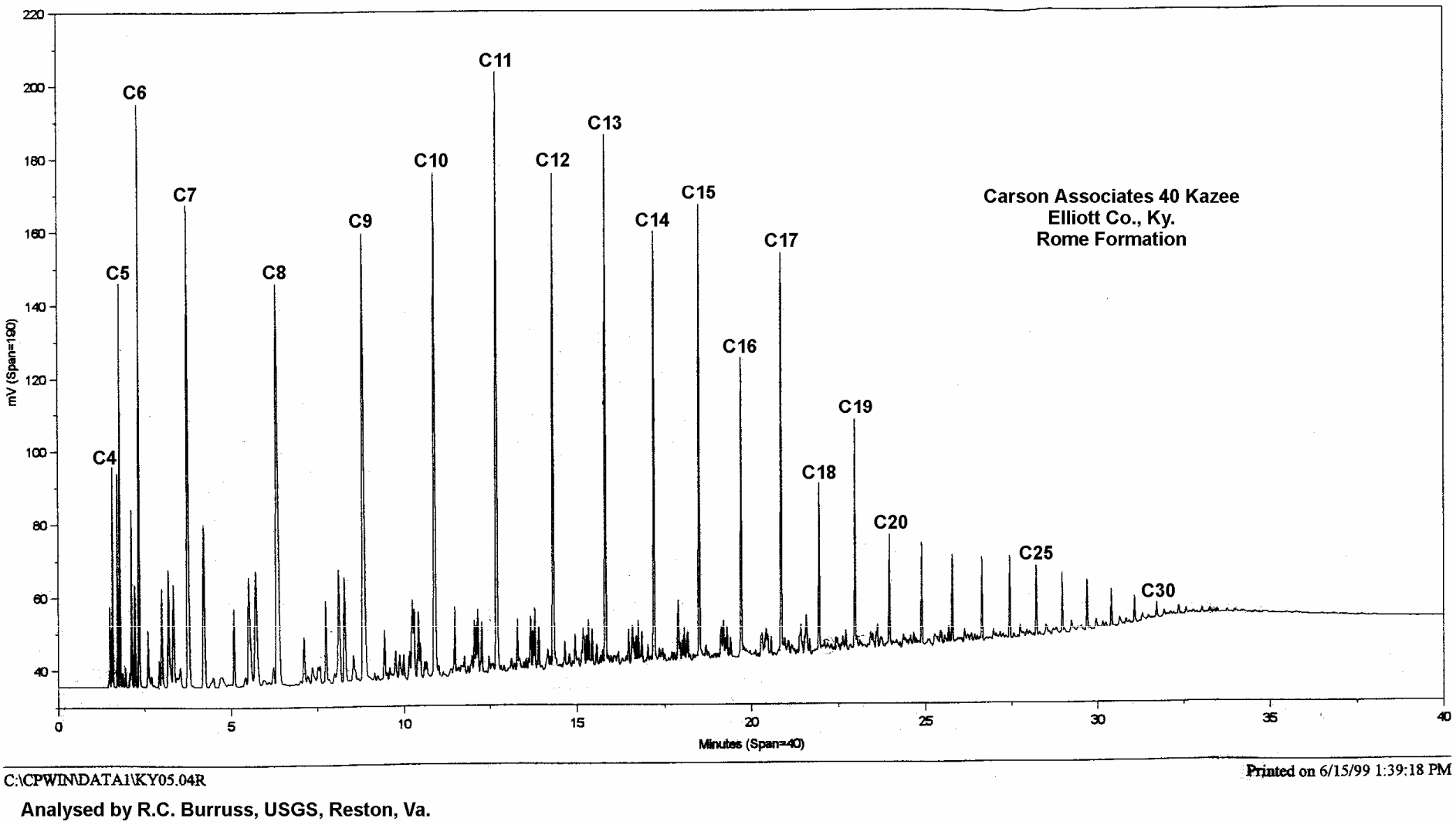


Figure 7-4. Preliminary gas chromatograph analysis for Rome Formation condensate from the Carson Assoc. 40 Kazee well, Elliott Co., Ky. Carbon number of hydrocarbons identified are labeled. Note the predominance of odd-carbon number compounds in the C11-C19 range, and absence of pristane and phytane peaks. These are characteristics of Ordovician (and possibly Cambrian) sourced hydrocarbons. Data courtesy of USGS and Equitable Resources (confidential).

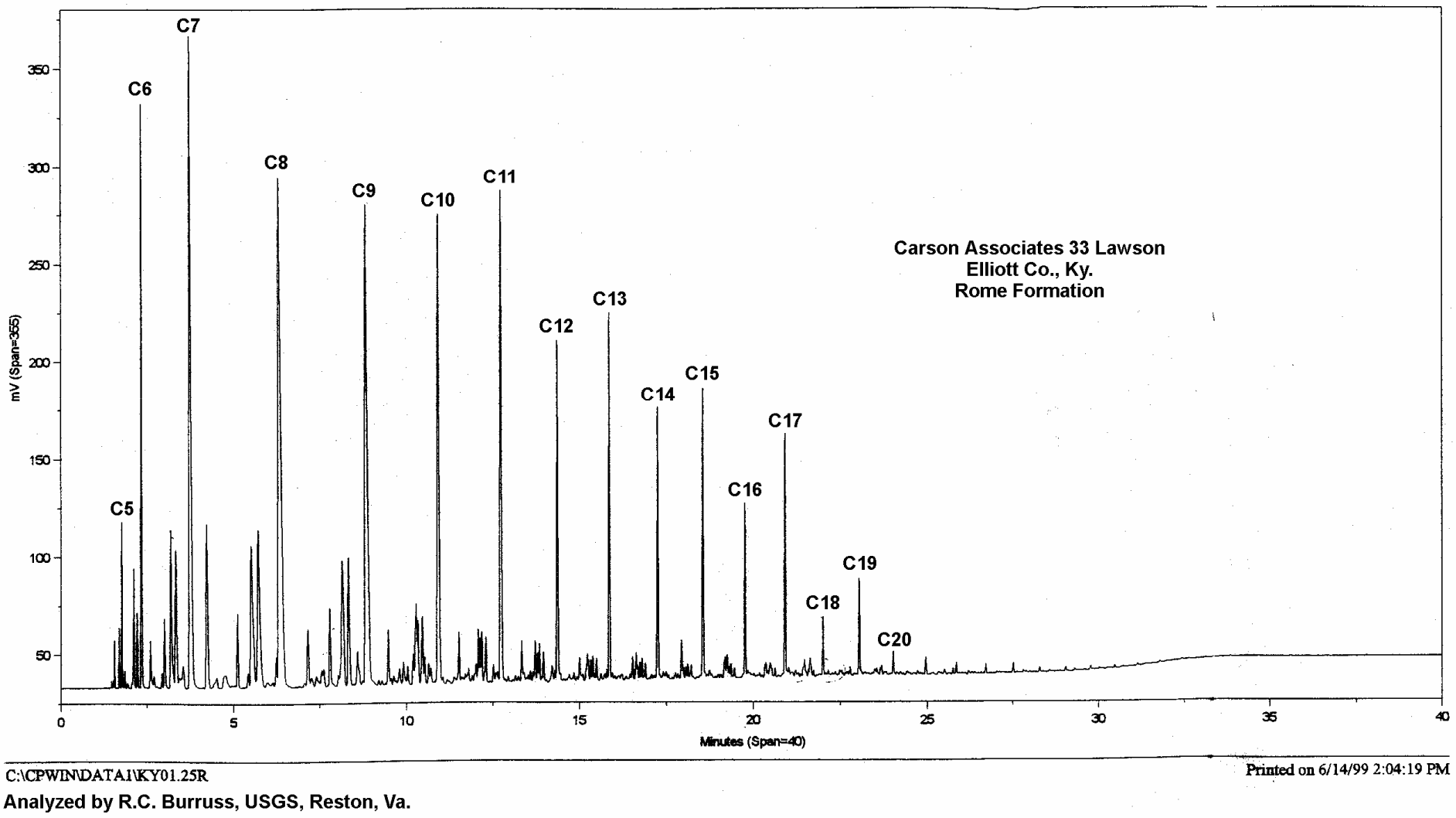


Figure 7-5. Preliminary gas chromatograph analysis for Rome Formation condensate from the Carson Assoc. 33 Lawson well, Elliott Co., Ky. Carbon number of hydrocarbons identified are labeled. Note predominance of odd-carbon number compounds in the C11-C19 range, and absence of pristane and phytane. These are characteristics of Ordovician (and possibly Cambrian) sourced hydrocarbons. Data courtesy of USGS and Equitable Resources (confidential).

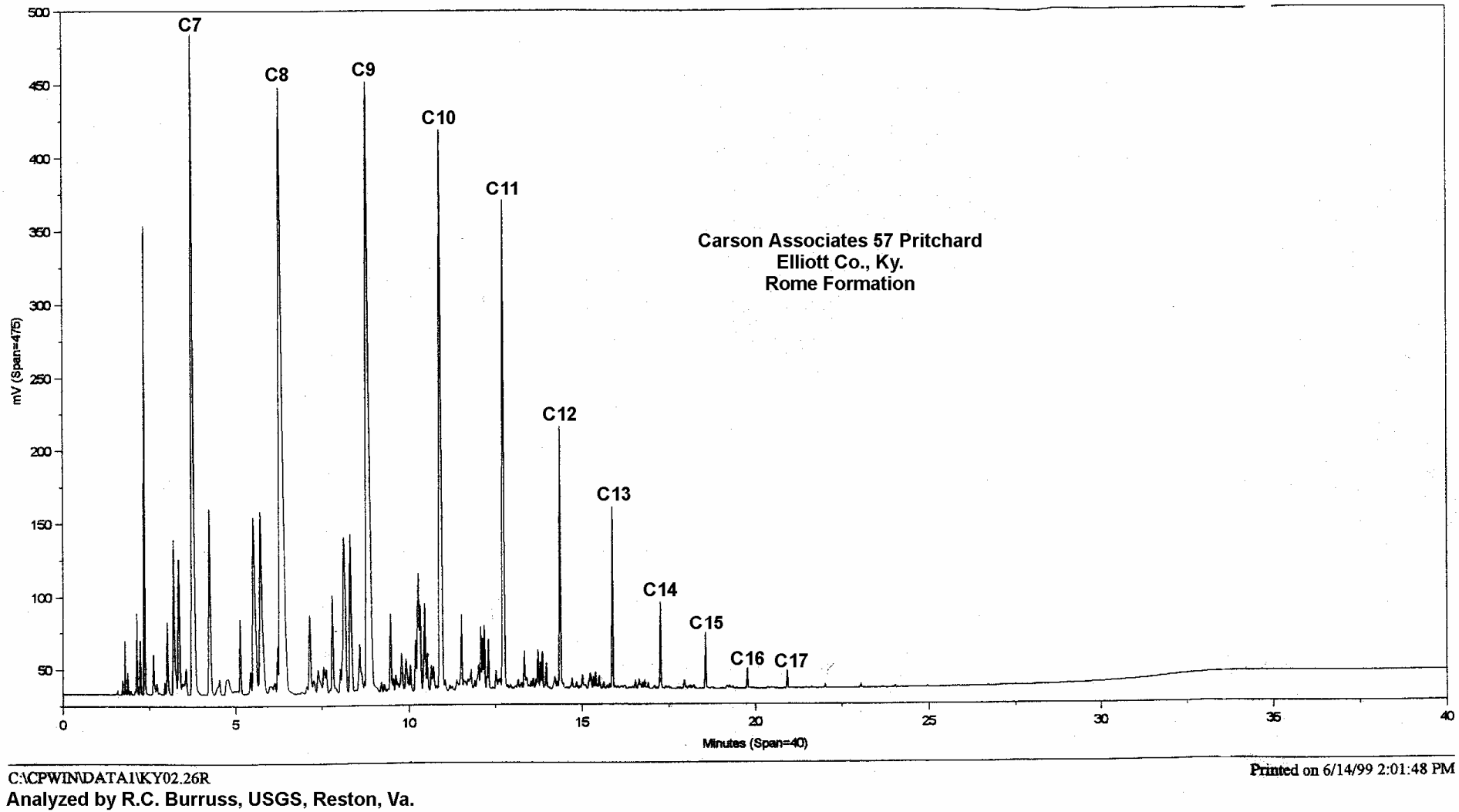


Figure 7-6. Preliminary gas chromatograph analysis for Rome Formation condensate from the Carson Assoc. 57 Pritchard well, Elliott Co., Ky. Carbon number of hydrocarbons identified are labeled. Odd-carbon number predominance is not apparent in this sample, but due to the lack of heavier hydrocarbons, this sampled needs further analysis. Data courtesy of USGS and Equitable Resources (confidential).

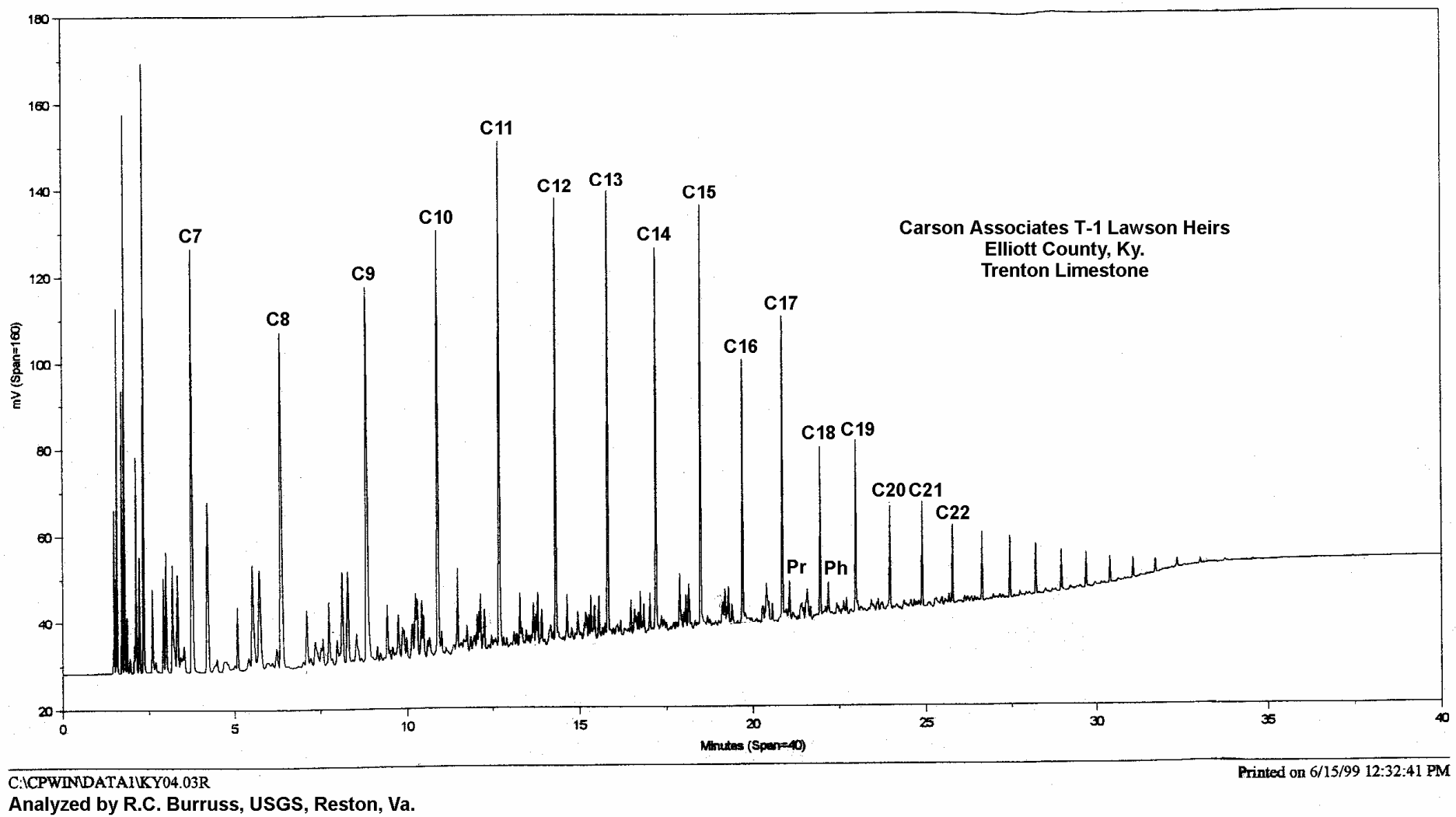


Figure 7-7. Preliminary gas chromatograph analysis for Trenton Limestone condensate from the Carson Assoc. T-1 Lawson Heirs well, Elliott Co., Ky. Carbon number of hydrocarbons identified are labeled. Note the predominance of odd-carbon number compounds in the C11-C19 range. Minor peaks for pristane and phytane are labeled. These are characteristics of Ordovician (and possibly Cambrian) sourced hydrocarbons. Data courtesy of USGS and Equitable Resources (confidential).

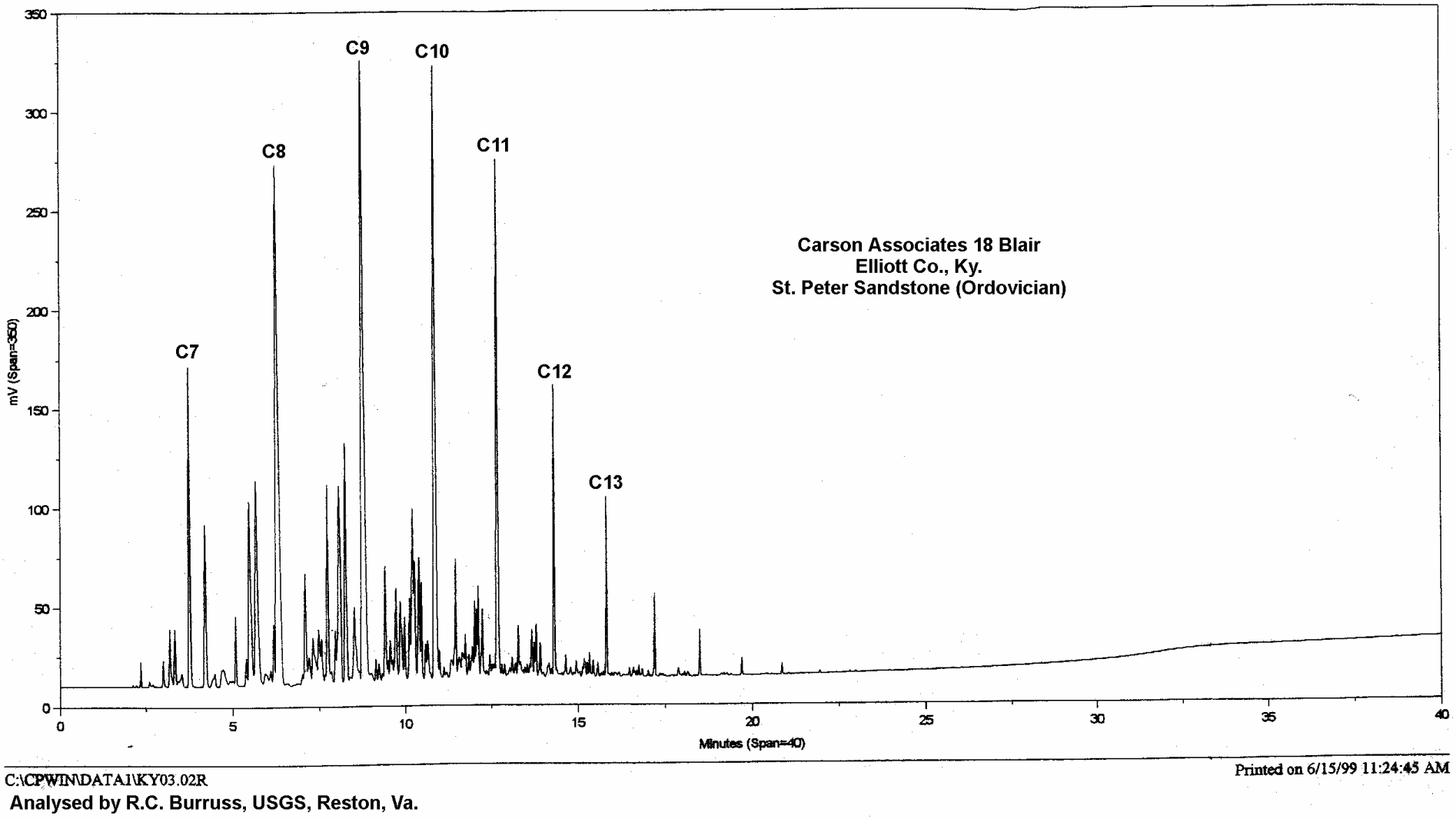


Figure 7-8. Preliminary gas chromatograph analysis for Ordovician St. Peter Sandstone condensate from the Carson Assoc. 18 Blair well, Elliott Co., Ky. Carbon number of hydrocarbons identified are labeled. Data courtesy of USGS and Equitable Resources (confidential).

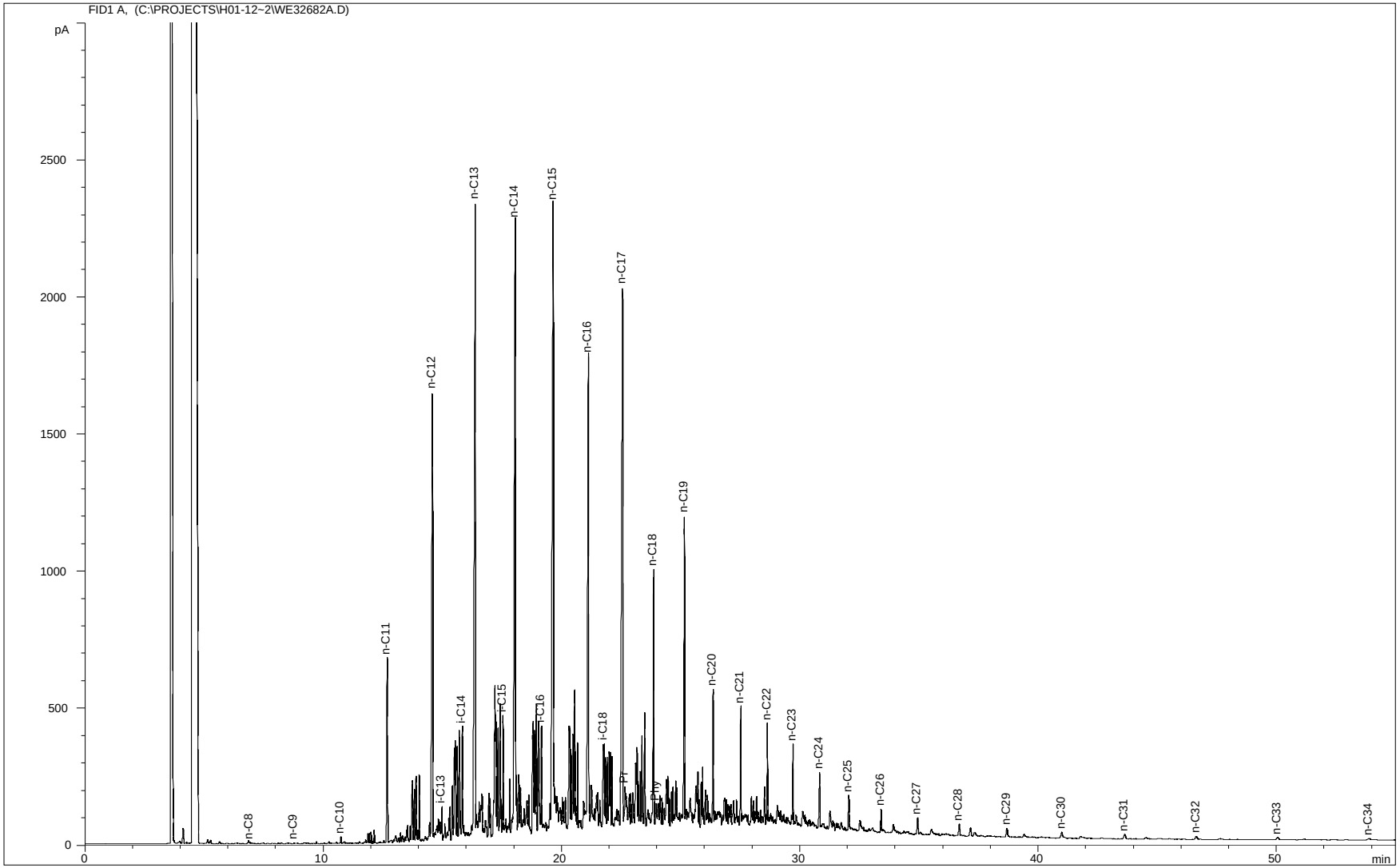


Figure 7-9. Whole extract gas chromatographic fingerprint from core sample of Rogersville Shale in the Exxon 1 Smith well at 11,161.5 ft. Note the predominance of odd-carbon number hydrocarbons, and small pristane (Pr) and phytane (Phy) peaks, characteristic of Ordovician and possibly Cambrian sourced oils. Data from Humble Geochemical, Houston, Tx., courtesy of USGS.

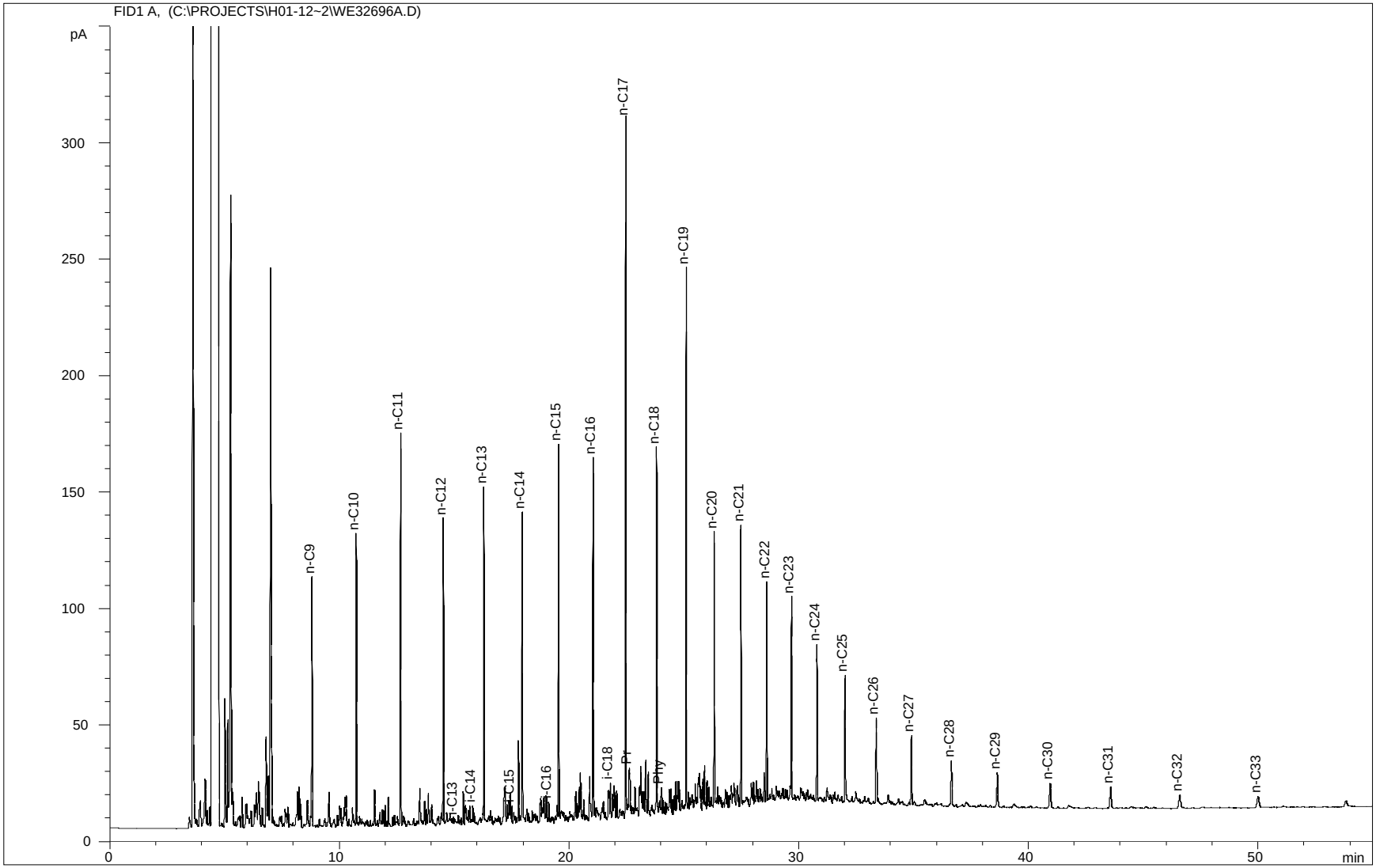
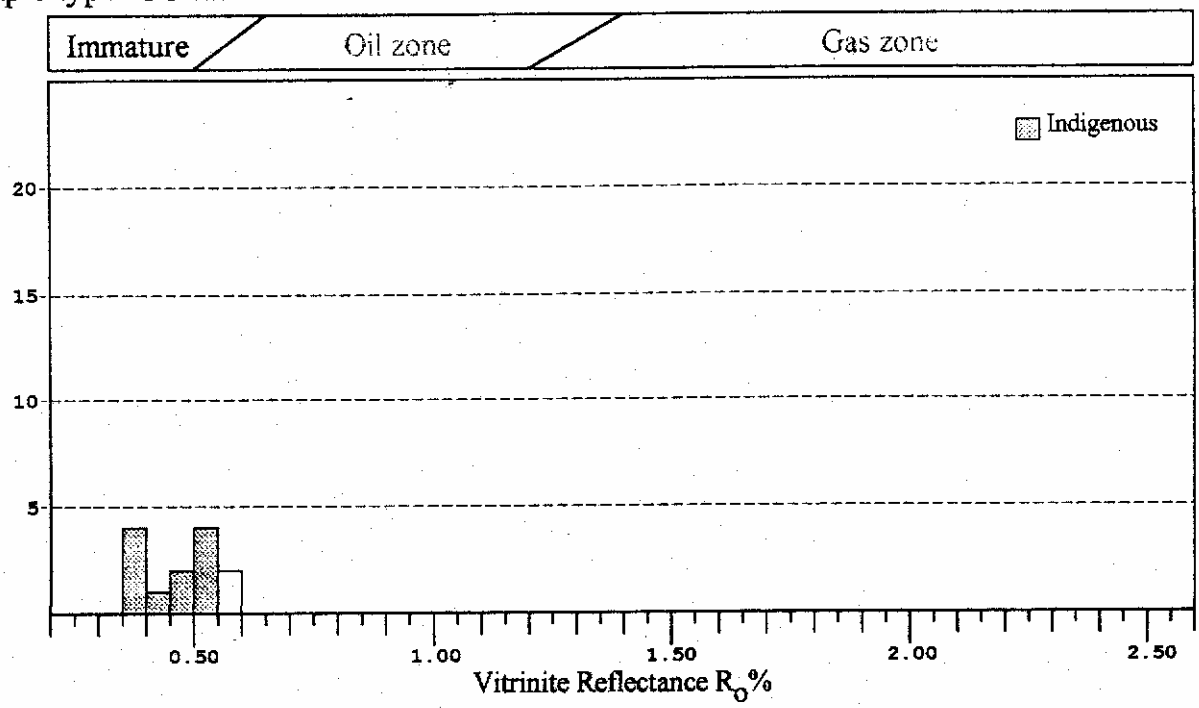


Figure 7-10. Whole extract gas chromatographic fingerprint from a core sample in the Texaco 1 Kirby well at 4,628.8 ft. Note the predominance of odd-carbon number hydrocarbons, and small pristane (Pr) and phytane (Phy) peaks, characteristic of Ordovician and possibly Cambrian sourced oils. Data from Humble Geochemical, Houston, Tx., courtesy of USGS.

Customer: ***USGS***
Well name: ***TEXACO #1 KIRBY, GARRARD, KY***
Sample ID: ***016-079-21048***
Mean depth (ft): ***4576***
Sample type: ***CORE***



Indigenous population statistics

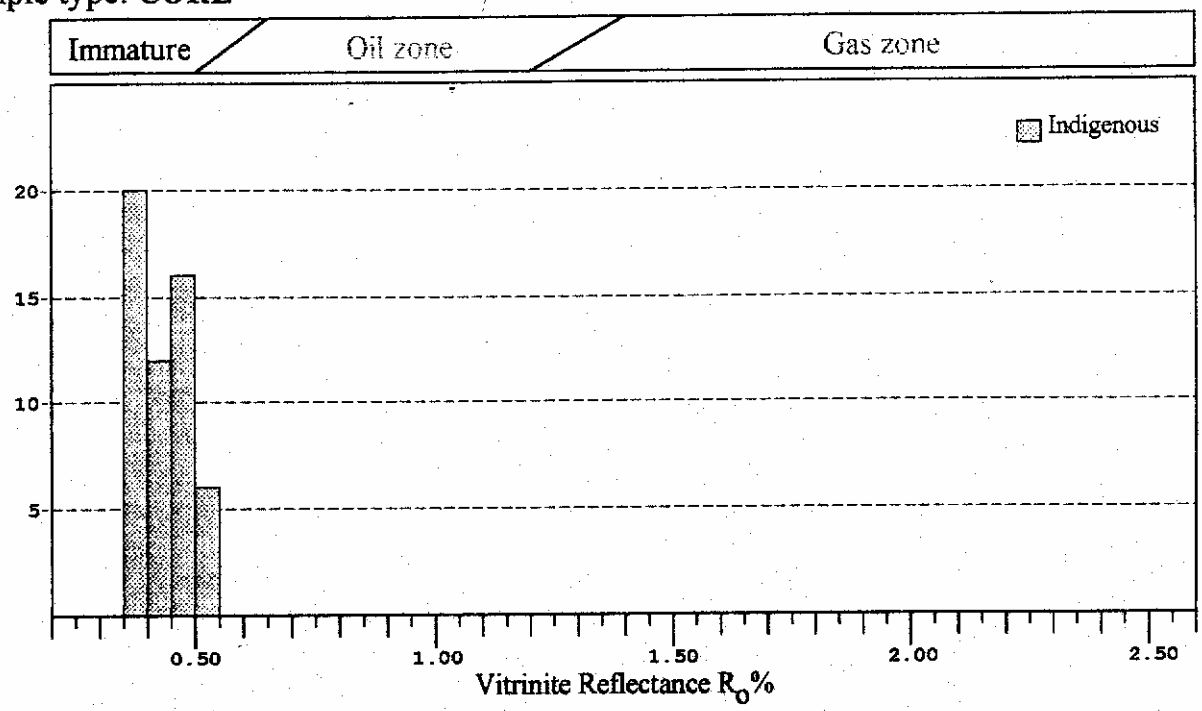
Mean: 0.45 Min: 0.35 Max: 0.54 Std. Dev.: 0.08 Count: 11

Total population statistics

Mean: 0.47 Min: 0.35 Max: 0.56 Std. Dev.: 0.08 Count: 13

Figure 7-11. Vitrinite reflectance histogram of "vitrinite-like" material from Rome Formation core at 4,576 ft in the Texaco 1 Kirby well, Garrard Co., Ky. Thermal maturity is immature, with a mean R_o of 0.45. The origin of the material measured is unknown, but it is not true vitrinite due to the age of the sample. Data courtesy of USGS.

Customer: ***USGS***
Well name: ***TEXACO #1 KIRBY, GARRARD, KY***
Sample ID: ***016-079-21048***
Mean depth (ft): ***4628***
Sample type: ***CORE***



Indigenous population statistics

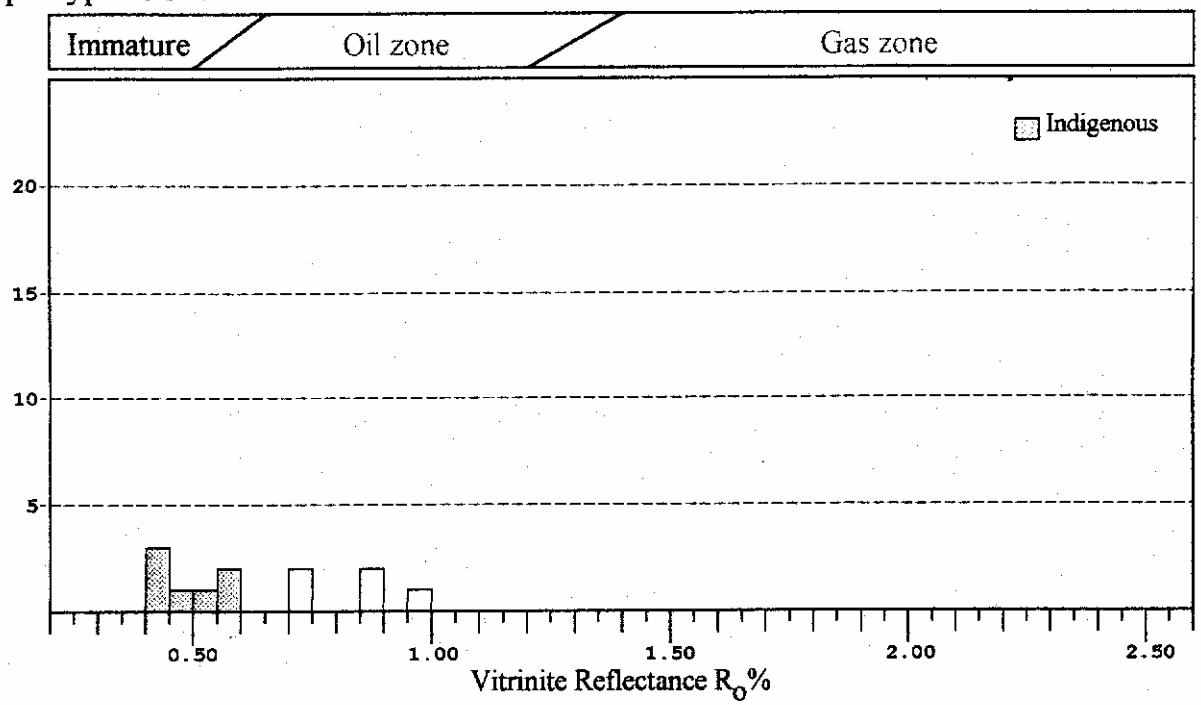
Mean: 0.43 Min: 0.36 Max: 0.52 Std. Dev.: 0.05 Count: 54

Total population statistics

Mean: 0.43 Min: 0.36 Max: 0.52 Std. Dev.: 0.05 Count: 54

Figure 7-12. Vitrinite reflectance histogram of "vitrinite-like" material from Rome Formation core at 4,628 ft in the Texaco 1 Kirby well, Garrard Co., Ky. Thermal maturity is immature, with a mean R_o of 0.43. The origin of the material measured is unknown, but it is not true vitrinite due to the age of the sample. Data courtesy of USGS.

Customer: ***USGS R. RYDER***
Well name: ***TEXACO NO. 1 TIPTON***
Sample ID: ***6375.5***
Mean depth (ft): ***6375.5***
Sample type: ***CORE***



Indigenous population statistics

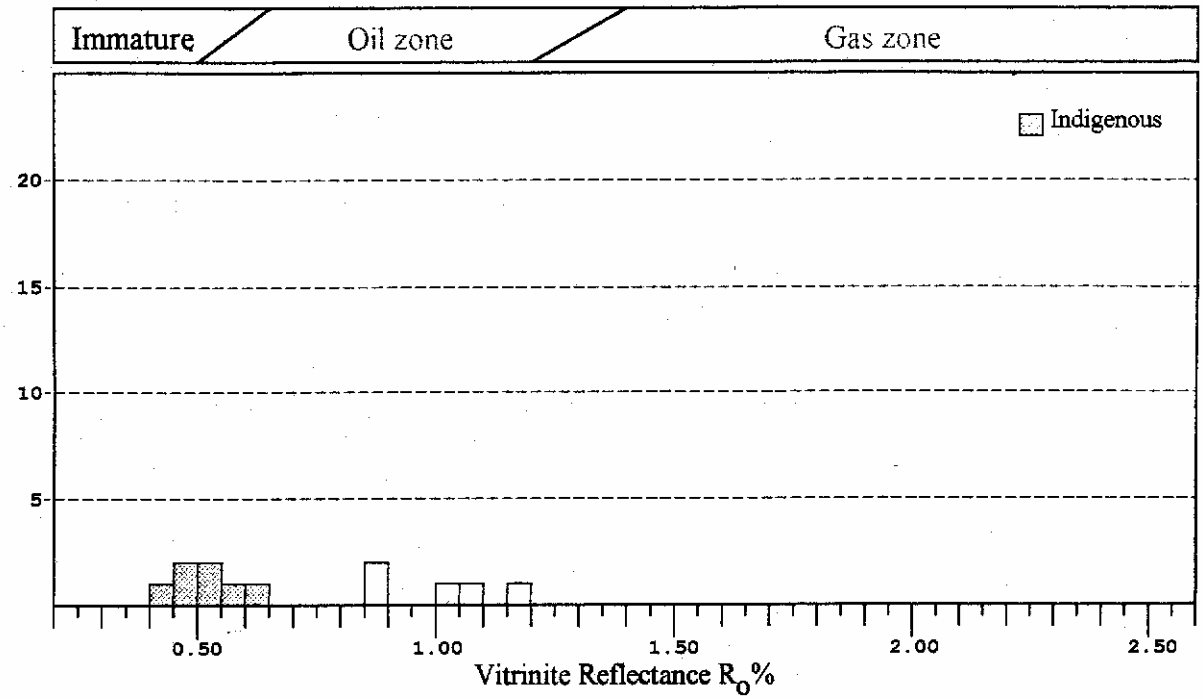
Mean: 0.49 Min: 0.44 Max: 0.56 Std. Dev.: 0.06 Count: 07

Total population statistics

Mean: 0.63 Min: 0.44 Max: 0.97 Std. Dev.: 0.19 Count: 12

Figure 7-13. Vitrinite reflectance histogram of "vitrinite-like" material from Rome Formation core at 6,375.5 ft in the Texaco 1 Tipton well, Estill Co., Ky. Thermal maturity is immature to possibly the lower oil window, with a mean R_o of 0.49. The origin of the material measured is unknown, but it is not true vitrinite due to the age of the sample. Data courtesy of USGS.

Customer: ***USGS R. RYDER***
Well name: ***TEXACO NO. 1 TIPTON***
Sample ID: ***6385***
Mean depth (ft): ***6395***
Sample type: ***CORE***



Indigenous population statistics

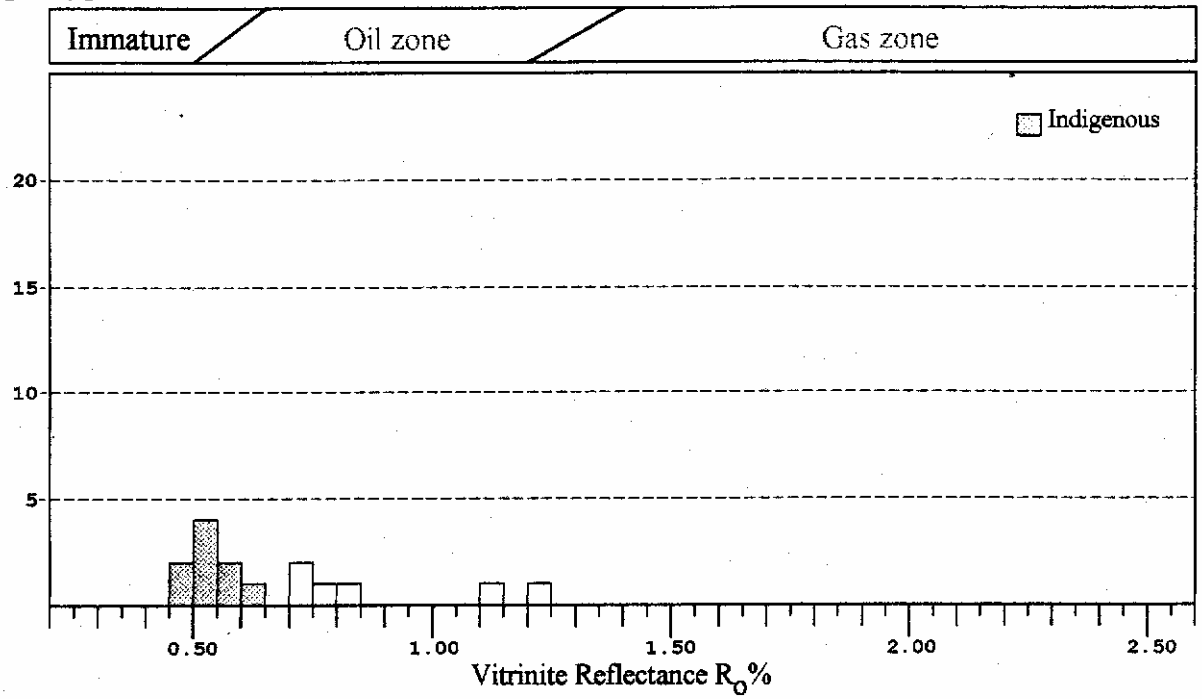
Mean: 0.51 Min: 0.44 Max: 0.60 Std. Dev.: 0.06 Count: 07

Total population statistics

Mean: 0.71 Min: 0.44 Max: 1.17 Std. Dev.: 0.27 Count: 12

Figure 7-14. Vitrinite reflectance histogram of "vitrinite-like" material from Rome Formation core at 6,395 ft in the Texaco 1 Tipton well, Estill Co., Ky. Thermal maturity is immature to possibly the lower oil window, with a mean R_o of 0.51. The origin of the material measured is unknown, but it is not true vitrinite due to the age of the sample. Data courtesy of USGS.

Customer: ***USGS R. RYDER***
Well name: ***TEXACO NO.1 TIPTON***
Sample ID: ***6389.5***
Mean depth (ft): ***6389.5***
Sample type: ***CORE***



Indigenous population statistics

Mean: 0.53 Min: 0.45 Max: 0.63 Std. Dev.: 0.06 Count: 09

Total population statistics

Mean: 0.68 Min: 0.45 Max: 1.20 Std. Dev.: 0.23 Count: 15

Figure 7-15. Vitrinite reflectance histogram of "vitrinite-like" material from Rome Formation core at 6,389.5 ft in the Texaco 1 Tipton well, Estill Co., Ky. Thermal maturity is immature to possibly the lower oil window, with a mean R_o of 0.53. The origin of the material measured is unknown, but it is not true vitrinite due to the age of the sample. Data courtesy of USGS.