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GEOCHEMICAL CHARACTERIZATION OF THE LOWER PENNSYLVANIAN MORROW SHALE IN THE ANADARKO BASIN OF OKLAHOMA

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GEOCHEMICAL CHARACTERIZATION OF THE LOWER PENNSYLVANIAN MORROW SHALE IN THE ANADARKO BASIN OF OKLAHOMA

A THESIS APPROVED FOR THE
CONOCOPHILLIPS SCHOOL OF GEOLOGY AND GEOPHYSICS

BY

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Dedicated to the memory of my father, Turgut Sümer, whom I still miss every day… to my mother, Feriha Sümer, who has been there for me and supported me through all my life… and to Arcan, for his love and unconditional support. You bring comfort and joy into my life…

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Abstract

The Morrow Formation is one of the most widespread units of Early Pennsylvanian time in the Anadarko Basin. While the Morrow Sandstone has been one of the most productive oil and gas reservoirs since the 1950s, the Morrow Shale has become important recently due to developments in the unconventional shale sector. The publicly available geochemical information about this formation is very limited. Therefore, this study investigates the geochemical characteristics of the Morrow Shale in the Anadarko Basin and will help to fill the gap in the literature on geochemical characteristics of the Morrow Formation.

Fifteen Morrow source rock samples from different parts of the Anadarko Basin and source rock samples from two different wells in the area were geochemically characterized by means of bulk geochemical and biomarker data. The Rock-Eval Pyrolysis data including Total Organic Carbon (TOC), S_1 (free hydrocarbons already present in the source rock), S_2 (potential generative capacity), T_{max} (maturity level of the sample) and hydrogen and oxygen indexes (HI and OI) indicate that the Morrow source rocks are fair to good source rocks, characterized by the Type-III kerogen that has gas generating capacity and is thermally mature.

Biomarker analyses of the source rocks extracts were conducted by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The aliphatic and aromatic biomarker results demonstrated that the Morrow Shale is composed of mixed organic matter with more pronounced terrestrial input than marine. Depositional conditions were interpreted as a near-shore/transitional depositional environment which was subjected to periodic terrigenous influx by fluvial activities.

The abundance of the C_{29} 17(α)-hopane in some of the rock extracts was interpreted as increasing carbonate content or evaporitic conditions in the depositional environment. Alternatively, relatively high concentrations of rearranged hopanes (18(α)-30-norneohopane and 17(α)-diahopane) reveals that the Morrow was deposited under clay-rich, brackish/freshwater conditions of a suboxic depositional environment.

The tentative presence of 18α(H)-oleanane was confirmed in the Morrow source rock samples. 18α(H)-Oleanane is a biomarker derived from angiosperm plants and commonly used as an age-specific biomarker for Cretaceous and younger rocks. Its presence in pre-Cretaceous rocks is uncommon but has been confirmed by Moldowan et al. (1994), Peters et al. (1999) and Taylor et al. (2006). Moreover, 1,2,7-trimethylnaphthalene (1,2,7-TMN), a proposed alteration product of 18α(H)-oleanane, or oleanane type marker, was identified in all of the studied samples. The presence of 18α(H)-oleanane and 1,2,7-TMN in the Morrow source rocks suggests that they are either derived from angiosperms that evolved long before the Cretaceous or were derived from a sister-group of angiosperms that share common characteristics with the angiosperms and were capable of synthesizing β-amyrin or other related compounds.

Demethylated hopanes such as 25-norhopanes (NHP), 25,28,30-trisnorhopane (TNH), 25,30-bisnorhopane are commonly found in biodegraded oils and their presence in the rock extracts is unusual as they are not found in the pyrolysis products of the kerogen and therefore they should be present in the sediments as free hydrocarbon. This study confirms the tentative presence of demethylated hopanes in multiple source rock samples and is interpreted as paleo-seepage from an ancient heavily biodegraded reservoir or *in-situ* biodegradation of the oil at the fissures and fractures of the Morrow Shale.

Finally, the presence of pyrolytic polycyclic aromatic hydrocarbons (PAHs) in the Morrow source rocks revealed that paleo-wildfires were part of the terrestrial ecosystem during Early Pennsylvanian time revealed by high concentrations of pyrene, fluoranthene, benzopyrenes, benzofluoranthenes, benzo(a)anthracene, triphenylene, and chrysene in the source rock extracts. The presence of cadalene, fluorene and dibenzofuran provide supporting evidence for the Morrow being a freshwater/brackish water shale deposited under fluvio-deltaic conditions.

Chapter 1: Introduction

The Morrow Shale is a Lower Pennsylvanian shale with discontinuous sandstone reservoirs and thin limestone units. It is a widely distributed formation deposited within the states of Arkansas, Oklahoma, Texas, Kansas, Colorado, Nebraska, Wyoming and South Dakota (Andrews, 2008). The Morrow Formation has an asymmetric character with over 4000 ft thick sediments in the deep trough of the Anadarko Basin and progressively thinning through the Panhandle with around 300 ft thick sediments (Adler et al., 1971). The Morrow Formation is a basal transgressive genetic sequence of Lower Pennsylvanian time (Higley et al., 2014). It is almost always overlain by the "Thirteen Finger Limestone" of the Atoka Formation and underlain by the Springer Formation (Andrews, 1999). However, the Morrow-Springer boundary has always been a controversial issue as it is also considered to be a regional unconformity surface.

The Morrow Shale is one of the important source rock units in the Anadarko Basin (Hatch et al., 1987). Average thickness of the Morrow Formation in Oklahoma is about 1500 ft and more than 60 percent of it is composed of shale and mudstone (Wang and Philp, 1997). The Morrow Shale is mainly characterized with type-III kerogen indicating that it is primarily gas-prone. Higley et al. (2014) mentioned that, based on an oral communication with Joseph Hatch in 2010, total organic carbon (TOC) values of Morrowan Shales from 14 wells in the Anadarko Basin ranged from 0.48 to 10.71 wt. % with average of 1.72 wt. %. Moreover, hydrogen index (HI) values range from 15 to 179 with an average of 46. According to Andrews (1999), the degree of maturation of the Morrow Formation varies with the depth. For instance, vitrinite reflectance value of the samples from the deeper Anadarko Basin exceeds 2.5% R_0 while through northwestern

Oklahoma, where the thickness significantly decreases, this value drops to 0.5% R_0 (Figure 1).

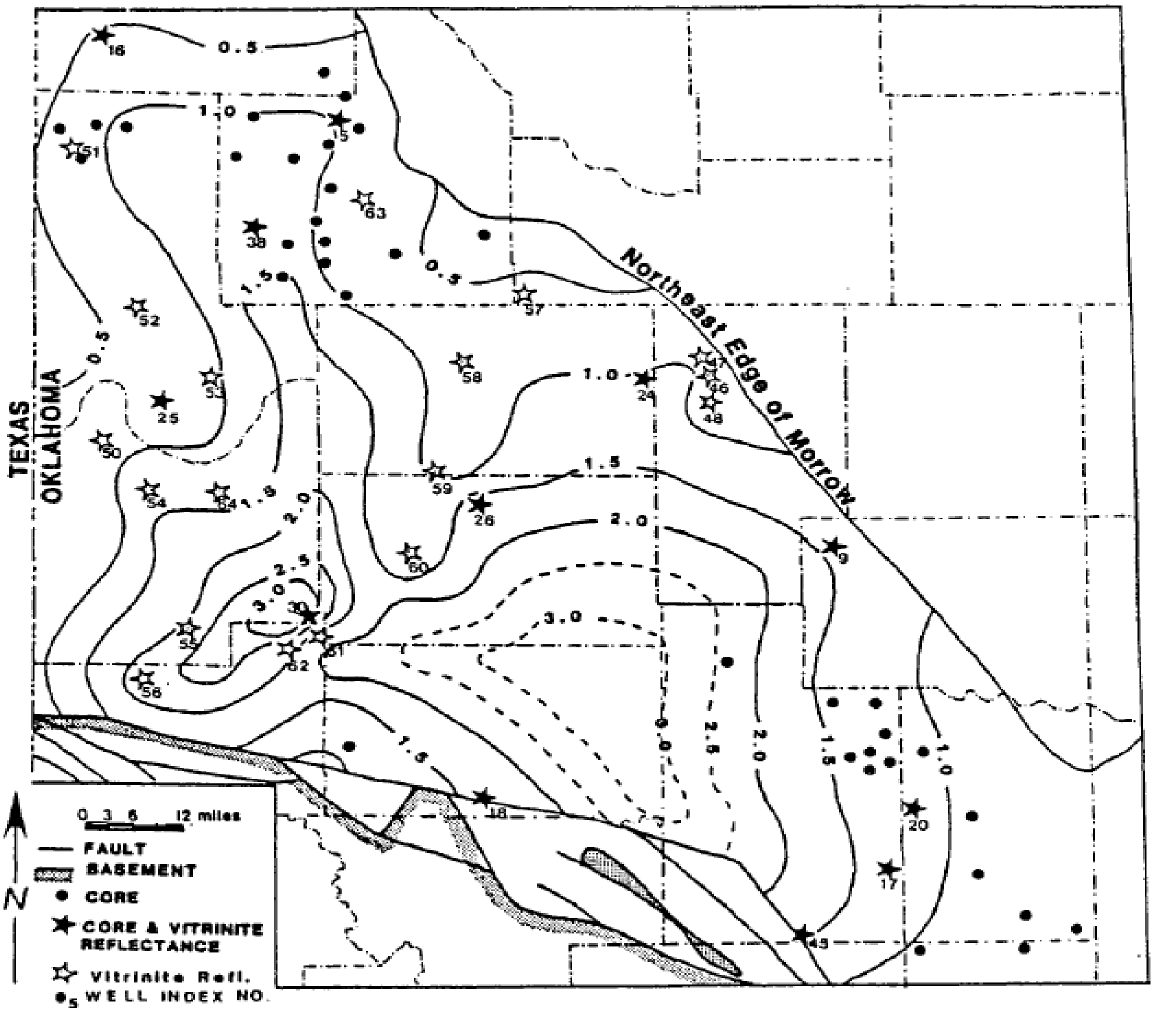


Figure 1. Map showing distribution of vitrinite reflectance of the Morrow sediments in the Anadarko Basin. Contour interval is 0.5% R_0 (Modified from Andrews, 1999).

The Morrow Sandstones, alternatively, have been one of the best conventional oil and gas reservoirs in the Anadarko Basin since the 1950s. These sandstones produce the highest amount of oil and gas among the Chesterian through Atokan Series (Mitchell, 2012). Hydrocarbon production is commonly sustained from numerous sandstone bodies within the formation. Cumulative oil and gas production from 14,000 Morrow wells in the Oklahoma and the Texas Panhandle is 550 million barrels of oil (MMBO) and 23 trillion cubic feet of gas (TCFG), respectively (Andrews, 2008). Moreover, Andrews, (2008) mentioned that the lower Morrow Sandstones has exceptional per-well basis performance numbers of oil and gas production with 39 thousand barrels of oil (MBO) and 1,643 million cubic feet of gas (MMCFG), respectively in the deeper Anadarko Basin. According to Information Handling Services (IHS) production data files for the Anadarko Basin, the percentage of cumulative gas and oil productions are 21% and 17% among the other formations in the Anadarko Basin (Mitchell, 2012) which makes it a very important conventional hydrocarbon reservoir.

There is very limited organic geochemical information in publicly available literature about the Morrow Formation in the Anadarko Basin. One of the main reasons for this is the formation in the study area does not outcrop (Andrews, 1999). Most of the drilling activity has been carried out by private oil companies who are unlikely to supply their results and interpretations with others. The present study provides a detailed geochemical analysis of the Morrow Shale within the Anadarko Basin. The characterization is carried out by using bulk geochemical data and biomarker information produced from the Morrow source rocks. The core samples used in this study were gathered from different locations of the Anadarko Basin and analyzed by using GC, GC-MS, GCMS-MS and Rock-Eval pyrolysis. The purpose of this study is to carry out a comprehensive geochemical analysis of the Morrow Formation within the Anadarko Basin and to undertake a regional geochemical characterization of the formation by use of bulk geochemical parameters, such as TOC and Rock Eval pyrolysis, and biomarker data. A secondary objective of this study is to discuss the possible origin of oleanane and some of the demethylated hopane derivatives in the Morrow Shale.

Chapter 2: Geological Background

2.1 Geologic History of the Anadarko Basin

The asymmetric shaped Anadarko Basin, located in the southern Midcontinent, is the deepest interior cratonic basin within North America, with almost 40,000 ft thick Paleozoic sedimentary rocks overlying 20,000 ft thick Cambrian igneous rocks at the southern margin of the basin (Johnson, 1989). The Anadarko Basin is bounded by major uplifts such as Wichita and Amarillo Uplift on the South, Arbuckle Uplift on the Southeast, Nemaha Uplift on the East, Central Kansas Uplift on the North and Cimarron and Las Animas Arch to the West (Ball et al., 1991; Figure 2). The basin strikes Northwest-Southeast and is structurally deepest at its southern margin (Garner and Turcotte, 1984). Moderately dipping reverse faults truncate the basin at the South and shifted crystalline igneous rocks of the Wichita Mountains over Paleozoic sedimentary rocks (Garner and Turcotte, 1984).

The Anadarko Basin has a complex depositional history. The evolution of the Anadarko Basin has been divided into four main phases by most people studying tectonic and structural events of the basin through its geological history. Johnson (1989), summarized these four stages as follows: (1) The Precambrian to Middle Cambrian crustal consolidation during which excessive igneous activity took place in the region. During this period, igneous rocks intruded in the Wichita Uplift area, and formed the basement rocks of today’s southern margin of the Anadarko Basin. (2) The Late Cambrian to Mississippian early epeirogenic uplift phase during which thick, shallow marine sedimentary deposition occurred in a broad epicontinental sea in the Oklahoma Basin. (3) The Pennsylvanian period is the third stage during which breakthrough changes occurred in the Anadarko Basin. During the Pennsylvanian epeirogeny, a series of major uplifts created smaller basins that were formed as a result of breakup of the Oklahoma Basin. The Anadarko Basin was formed during this episode. (4) The Permian through Holocene includes a late epeirogenic stage during which the basin was filled with Permian red beds, evaporites and carbonates and it was subsequently followed by deposition of thin Post-Permian strata across the Anadarko Basin.

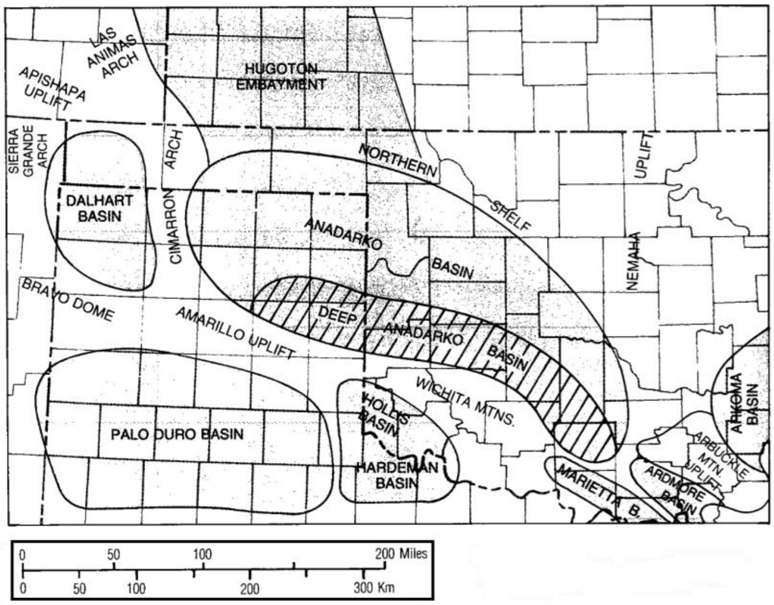


Figure 2. Location Map of the Anadarko Basin (Modified after Johnson 1989)

The Anadarko Basin is located within the southwestern part of the Southern Oklahoma Aulacogen (SOA) which is a Northwest-trending failed rift arm of a Cambrian triple junction (Buckey, 2012). Major structures associated with SOA are the Wichita-Amarillo Uplift, the Arbuckle Uplift and the Anadarko Basin (Buckey, 2012). The SOA was initiated in the latest Precambrian to earliest Cambrian time as a result of the opening of the ancestral Atlantic. This period was marked by extensive igneous emplacement and deposition of thousands of feet thick volcanic and metamorphic rocks about 1.4 billion years ago (Feinstein, 1981; Johnson, 1989). These rocks form the basement of the

Anadarko Basin and underlie a thick sedimentary succession of Paleozoic strata. The Reagan sandstone, which is composed of gravel and sand grains that were eroded from the igneous basement, overlies the igneous basement in the Anadarko Basin (Feinstein, 1981). The Reagan sandstone is overlain by the Arbuckle group which is predominantly a carbonate and dolomite section deposited in a shallow marine depositional environment (Tsiris, 1983). The depositional environment drastically changed during the middle to upper Ordovician which resulted in excessive clastic sedimentary rock deposition in the trough. These clastics are represented as the Simpson Group (Tsiris, 1983). Formation of the Simpson Group was followed by deposition of the Viola Limestone, Sylvan Shale, Hunton Group and Woodford Shale (Johnson, 1989). During Mississippian time, the Oklahoma trough was reactivated and as a result, more than 5500 ft thick of black shale was deposited in the deeper parts of the aulacogen (Tsiris, 1983). The stratigraphic column of the Anadarko Basin is shown in Figure 3.

The Pennsylvanian period was marked by major changes in the Anadarko Basin (Johnson, 1989). The North American Plate collided with the Gondwana Plate along the Ouachita trough and resulted in a change of the tectonic style of the basin from extension to compression (Wang and Philp, 1997). Intense tectonism resulted in the formation of a series of horsts and grabens in the region and they divided the Anadarko Basin into several smaller basins. The Amarillo-Wichita Mountains were uplifted during this period, and at the North of this uplift, thick Pennsylvanian sediments were deposited as a result of the high subsidence and sedimentation rate (Wang and Philp, 1997; Figure 4). Donovan et al. (1983) proposed that the sedimentation rate during Pennsylvanian was as high as 3000 ft. per million years in the Ouachita Mountain area.

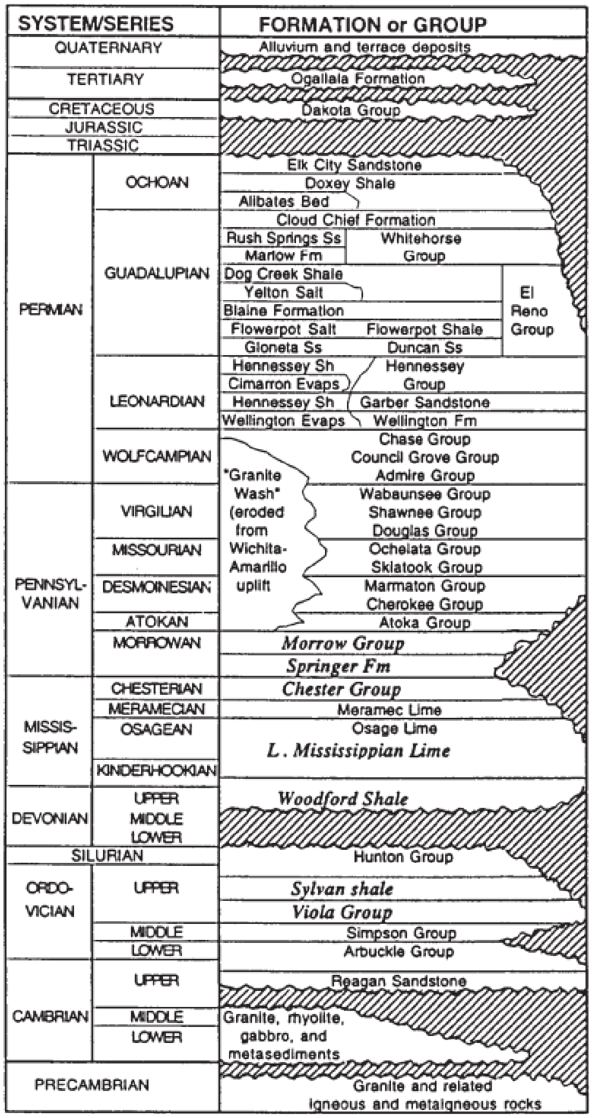


Figure 3. Stratigraphic column of the Anadarko basin (Thicknesses of formations are not to scale; Wang and Philp, 1997)

Epirogenic movement in the basin continued during the Permian through Holocene. During this period, red beds, carbonates and evaporites were deposited in the Anadarko Basin. Most of the post-Permian deposits were eroded from the Rocky Mountains Uplift and deposited in the basin (Johnson, 1989; Wang and Philp, 1997). The Anadarko Basin became tectonically inactive by the end of the Permian time and preserved its configuration since that time (Tsiris, 1983).

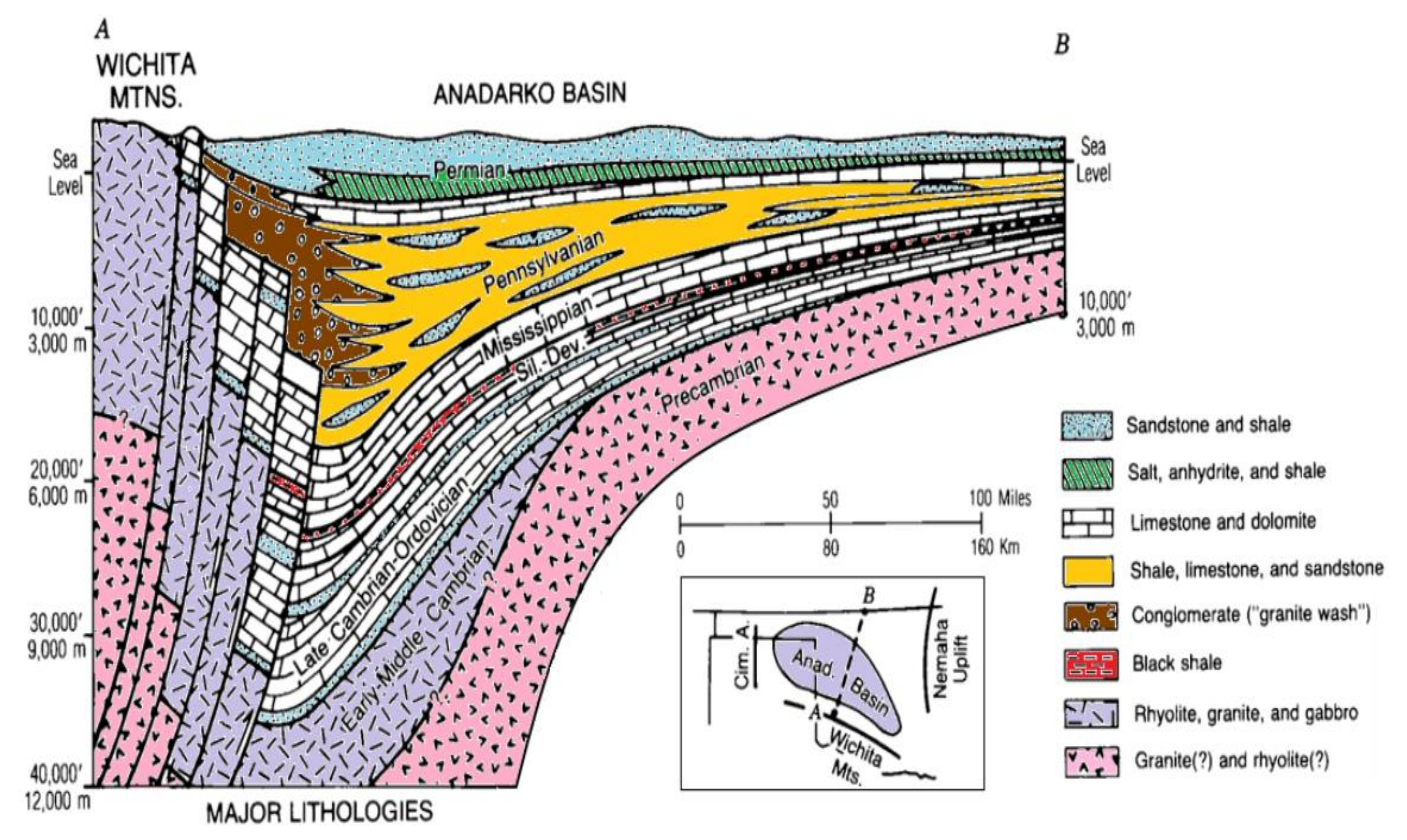


Figure 4. Diagrammatic North-South Cross Section of the Deep Anadarko Basin (Modified from Ball et al., 1991)

2.2 Previous Studies on the Morrow Formation

The Morrow formation was first named by Adams and Ulrich (1905) near the village of Morrow in Washington County, Arkansas (Curtis and Ostergard, 1980). They defined the formation as shale, sandstone and limestone and the rank of the formation was raised to group by Purdue et al. (1904). The series rank for the Morrow was first used by Moore (1944), who also proposed that the Morrow Series marks the beginning of the Pennsylvanian time in the Mid-Continent.

After its discovery, the first studies on the Morrow Formation were mainly for understanding its lithological characteristics. Thompson (1944) geologically described a Morrowan stratigraphic section found in Kearny County, Kansas. Maher and Collins (1953) prepared a map showing the thickness and distribution of the Morrowan age sediments in Southeast Colorado and adjacent areas. Barby (1956) briefly described different lithofacies of the Morrowan series in Beaver County, Oklahoma. In the same year, Totten (1956) divided the Morrow Formation into two as Upper Morrow and Lower Morrow in the Texas and the Oklahoma Panhandles. Abels (1958) studied subsurface lithofacies of the Morrowan Series in the northern Anadarko Basin and discussed the stratigraphic relationship of the Morrow with the underlying and overlying formations. The Oklahoma City Geological Society published two volumes of production index data that compiled some basic hydrocarbon production statistics of the Morrow and other gas fields in the Oklahoma and Texas Panhandles. Barrett (1964) studied subsurface geology of the Morrowan rocks in central and southern Beaver County, Oklahoma and investigated the Morrow in detail. He prepared different cross-sections of the Morrow, correlated the Morrow Formation throughout the county and subdivided it into Zones A, B and C based on its lithofacies. The effects of regional and local tectonics on the Morrow Formation were studied by Forgotson et al. (1966). The authors proposed that Pennsylvanian tectonics had a major impact on sedimentological characteristics of the Morrow. There were several studies that discussed subsurface geology and the depositional history of the Morrow Formation. For example, Arro (1965) interpreted the Morrow sandstone reservoirs as beach and shallow-marine bar deposits in the Oklahoma Panhandle while Swanson (1979) suggested that the Morrow Sandstones were deposited in a coastal-plain fluvial to deltaic environments. The author also identified deltaic sedimentation and point-bar reservoirs of the Morrow in the Anadarko Basin in order to provide help to the local exploration studies. Rascoe and Adler (1983) described the regional stratigraphy and facies relationships of the Upper Morrow in the Mid-Continent. One year later, Orchard and Kidwell (1984) studied the Morrow Formation in the Sorrento Field, Colorado and made a detailed description of the geological structures and reservoir facies in it. In the same field, Sonnenberg (1985) interpreted the productive the Morrow Sandstones as fluvial valley-fill deposits, consisting mainly of channel sandstones based on the subsurface mapping. The author added that the paleo-tectonic structures influenced the Morrow depositional patterns.

The sequence stratigraphy of the Morrow Formation has been studied since the 1980s. For instance, Emery and Sutterlin (1986) conducted some reservoir analysis and delineated the sand-body geometry and heterogeneity of the Morrow in the Lexington Field, Kansas with the help of some basic sequence stratigraphic principles. Krystinik et al. (1987) used some core and well-log data to differentiate coarse and fine valley-fill facies in the incised valley fills in order to improve production data in the Colorado and

Kansas regions. Stratigraphy and depositional history of the Morrow Formation in the Colorado and Texas regions were studied in detail by Wheeler et al. (1990). The authors subdivided the formation in two based on the depositional environments and revealed the sequence stratigraphic relationship between the upper and lower Morrow zones. Bowen and Weimer (2003) conducted one of the most comprehensive sequence stratigraphic analyses of the Morrow incised valley fills in Northwest Oklahoma. The authors described an entire range of lowstand depositional systems from incised-valley-fill systems to deep-water basin-floor systems in the Morrow and described the facies change in different systems tracts. Finally, Andrews (2008) revealed the importance of the Morrow and Springer Formations in terms of very detailed oil and gas production data in the southern Midcontinent.

Prior to the 1970s, there were no geochemical studies available in the literature on the Morrow Formation in the Anadarko Basin mainly due to the fact that before 1970 geochemistry and related methods were not well established. However, there were some studies including organic geochemistry of deep wells in the Anadarko Basin, Oklahoma. Pusey (1973) reported that the average TOC content of the Morrow Shale in the Baden Well-1 in Oklahoma was 0.5%. Hood et al. (1975) found the level of organic metamorphism (LOM) in the upper unit of Shell Rumberger Well-5 as 14 which corresponds to approximately 2.1% vitrinite reflectance according to Tsiris (1983). Price et al. (1981) investigated Bertha Rogers-I well in Washita County, Oklahoma. They found that between 5402 and 5649 m depth, which corresponds to the Upper Morrow Shale, organic carbon content, carbonate content, bitumen ratio and vitrinite reflectance are approximately 0.9%, 7.8%, 35, and 1.9%, respectively. In the unpublished MS thesis of

Tsiris (1983), source rock characteristics of the Uppermost Morrow Shale in the Anadarko Basin, Oklahoma, were evaluated. Moreover, he tried to relate higher maturity levels with the amount of graphitization in this interval. Walker (1986) conducted hydrous pyrolysis experiments to study maturity of the Morrow Formation and identified diagenetic characteristics of the formation. Wenger and Baker (1986) studied variations in organic geochemistry of anoxic-oxic black shale and carbonates in the Pennsylvanian Midcontinent. Burruss and Hatch (1988) and Rice et al. (1988) studied Paleozoic source rocks in the Oklahoma Basin in terms of kerogen type and total organic carbon. According to Burruss and Hatch (1988), Pennsylvanian shales are one of the designated potential source rocks in the Anadarko Basin. In the unpublished MS thesis of Hubert (1995), pressure regime, burial history and source rock maturation of the Morrow Formation in the western Anadarko Basin was analyzed. Wang and Philp (2001) described the geochemical characterization of important oil and source rocks in the Anadarko Basin and identified characteristic biomarkers of the Morrow Formation. Higley et al. (2014) summarized thermal maturation and burial history of petroleum source rocks, in the Anadarko Basin, in Colorado, Kansas, Oklahoma, and Texas.

2.3 The Early Pennsylvanian World in North America

The Carboniferous period was around 359.2 Ma-299 Ma years ago. It is mainly divided into two subsystems, the Early Carboniferous (Mississippian) and the Late Carboniferous (Pennsylvanian) in North America. The Mississippian stratigraphy can be easily distinguished from the Pennsylvanian stratigraphy in North-America (Waggoner, 1996) in a way that the Mississippian environment was marine dominated and more tropical which led to thick carbonate successions through North America. The Pennsylvanian Period was dominated with alternating marine and terrestrial conditions by the effects of South Pole Glaciation which caused the deposition of extensive coal during this period.

The Late Carboniferous period is the time when the Pangea Supercontinent started to form as a result of closing of the Rheic Ocean as the Gondwana and the Laurussia continents approached and collided with each other (Golonka, 2000). The collision developed the Ouachita-Appalachian Orogeny in North America and other mountain belts in different part of the world such as Mauretinides in Africa and the Variscan mountains in Europe (Golonka, 2000). There was also a major transition in paleoclimate from a Mississippian tropical and humid world into the Pennsylvanian with more arid and cooler conditions with the effect of Late Paleozoic Glaciation (LPG) at the South Pole. This abrupt change in climatic conditions was associated with closing of the equatorial Rheic seaway which might have led to major disturbances in oceanic and atmospheric circulation pathways and eventually triggered extensive glaciation at the South Pole (Smith and Read, 2000; Figure 5). During the LPG period, excess sea water was trapped as ice sheets which caused sea level to drop drastically and lead to an increases in terrestrial environments and habitats. Changes in the ice sheet volume in the Pennsylvanian time caused periodic sea-level fluctuations which can be observed in the rock record as deposition of shallow marine and mixed depositional environment sediments in cyclothym depositional setting in North America (Smith and Read, 2000).

DiMichele et al. (2005) stated that “The Late Carboniferous-Early Permian time interval was the first cold climate interval in Earth history where the continents were

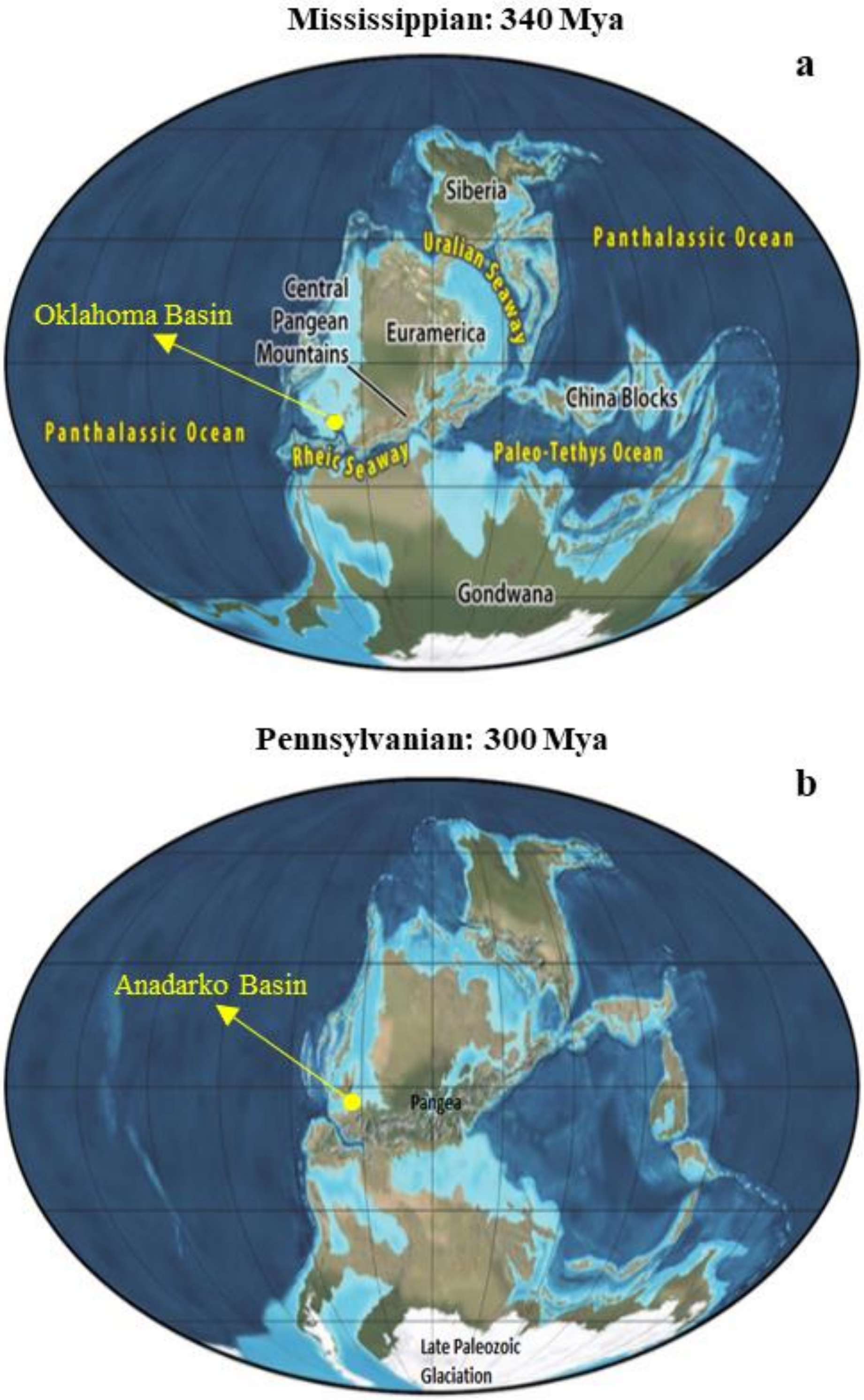


Figure 5. Paleogeographic maps of (a) The Late Mississippian (340 Mya) early icehouse and (b) the Late Pennsylvanian (300 Mya) peak icehouse (Modified after Montañez and Poulsen, 2013)

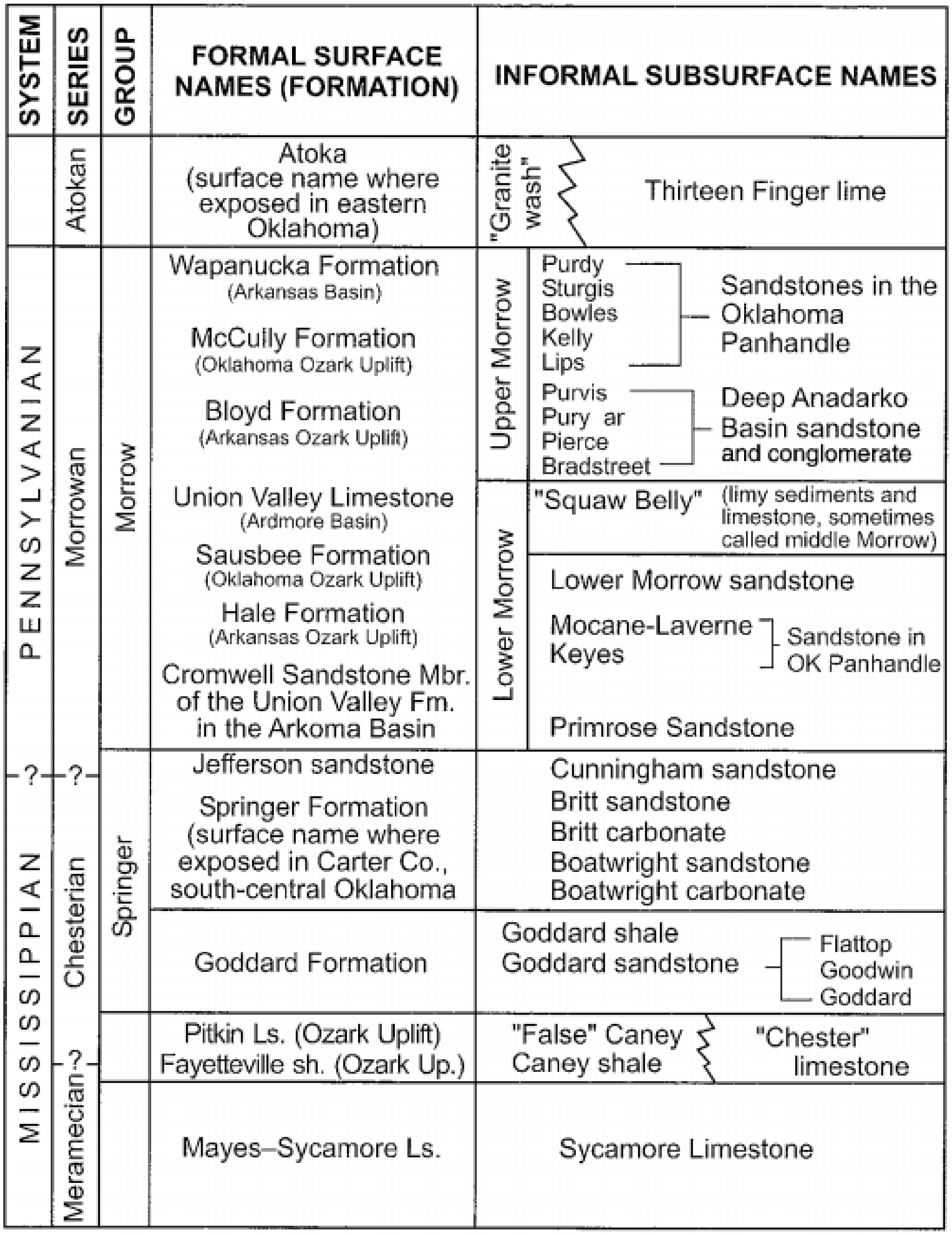
covered by vascular plants." During the Pennsylvanian Period, swamp forests were widespread and vascular plants such as ferns and lycopsids in the swamp forests were the main source of organic material for coal deposition which was deposited in excessive amounts in this period. The Serpukhovian extinction event occurred concurrently with formation of the Pangea Supercontinent and the Late Paleozoic Glaciation at the end of the Mississippian time (Powell, 2008). The collision of the Gondwana and the Laurussia continents decreased the net amount of coastline which in turn affected the diversity of marine habitats (Waggoner, 1996). McGhee et al. (2013) suggested that 39% of the marine fauna became extinct during the Serpukhovian extinction. In addition, freshwater clams and earliest ancestors of conifers appeared for the first time in history and the number of gastropods increased.

2.3 The Morrow Stratigraphy

The Morrow Formation is a basal transgressive unit that was deposited during the lower Pennsylvanian time (Forgotson et al., 1966). It is conformably overlain by the "Thirteen Finger Limestone" of the Atoka Formation and unconformably underlain by the Springer Formation (Andrews, 1999) in most of the Anadarko Basin. The Morrow-Springer boundary has always been a controversial issue as it is also considered to be a regional unconformity surface. According to Bowen and Weimer (2003), Mississippian carbonates are separated from the Morrow Formation by an angular unconformity which was formed as a result of the late Mississippian epeirogeny. Alternatively, Andrews (1995) suggested that in the shallower parts of the Anadarko Basin this stratigraphic relation between the Morrow and the Springer is completely conformable. Moreover, the

Pennsylvanian-Mississippian boundary is generally associated with the Morrow-Springer boundary although this may not be applicable elsewhere (Peace, 1989).

The Morrow sediments have not been formally subdivided into groups, formations or members in Oklahoma (Andrews, 1999). The formation is not exposed in the region and the facies are extremely variable within short distances both vertically and laterally (Abels, 1958). Thus, there are various informal subsurface names proposed by geologists (Figure 6). Some of the subdivisions were made based on lithology while the others were based on depositional environment, geological convenience or economic significance. For example, Forgotson et al. (1966) subdivided the formation as the Lower, Middle and Upper Morrow based on the lithology. According to Forgotson et al. (1966), the Lower unit is composed of terrestrial clastics, the Middle unit composed of marine limestone and shales and the Upper unit is only composed of shale. Benton (1973) studied the Morrow in Texas County, Oklahoma and subdivided the Morrow Formation into Upper and Lower zones and he suggested that the former was deposited in a fluvial environment and the latter was deposited in a marine environment. Shelby (1980), Curtis and Ostergard (1980) and Andrews (2008) subdivided the Morrow Formation based on the geological convenience and economic significance. They used a regionally extensive limestone unit, which is informally called Squaw Belly, to subdivide the formation and named the strata above the Squaw Belly as the Upper Morrow, and below it as the Lower Morrow Formation. In this study the name "Morrow Formation" is used for the rock succession from the top of the Mississippian Springer Formation to the bottom of the Atokan Thirteen Finger Limestone.



SYSTEM	SERIES	GROUP	FORMAL SURFACE NAMES (FORMATION)	INFORMAL SUBSURFACE NAMES	
	Atokan		Atoka (surface name where exposed in eastern Oklahoma)	"Granite wash"	Thirteen Finger lime
PENNSYLVANIAN	Morrowan	Morrow	Wapanucka Formation (Arkansas Basin) McCully Formation (Oklahoma Ozark Uplift) Bloyd Formation (Arkansas Ozark Uplift)	Upper Morrow	Purdy Sturgis Bowles Kelly Lips — Sandstones in the Oklahoma Panhandle Purvis Pury ar Pierce Bradstreet — Deep Anadarko Basin sandstone and conglomerate
			Union Valley Limestone (Ardmore Basin) Sausbee Formation (Oklahoma Ozark Uplift) Hale Formation (Arkansas Ozark Uplift) Cromwell Sandstone Mbr. of the Union Valley Fm. in the Arkoma Basin	Lower Morrow	"Squaw Belly" (limy sediments and limestone, sometimes called middle Morrow) Lower Morrow sandstone Mocane-Laverne Keyes — Sandstone in OK Panhandle Primrose Sandstone
?	?	Springer	Jefferson sandstone Springer Formation (surface name where exposed in Carter Co., south-central Oklahoma		Cunningham sandstone Britt sandstone Britt carbonate Boatwright sandstone Boatwright carbonate
MISSISSIPPIAN	Chesterian		Goddard Formation		Goddard shale Goddard sandstone — Flattop Goodwin Goddard
	?		Pitkin Ls. (Ozark Uplift) Fayetteville sh. (Ozark Up.)		"False" Caney Caney shale — "Chester" limestone
	Meramecian-?		Mayes–Sycamore Ls.		Sycamore Limestone

Figure 6. Formal and Informal Stratigraphic Nomenclature Chart of the Morrow formation in the Anadarko Basin (Andrews, 2008).

2.4 Depositional Environment of the Morrow Shale in Oklahoma

Within Oklahoma, the Morrow Formation was deposited under different depositional conditions, which caused diverse depositional facies in different basins

(Figure 7). In the Ardmore Basin, for example, the Morrow prevailed under deeper marine conditions with very fine grained silty sandstone with abundant glauconite, sponge spicules and the absence of shallow marine fossils (Andrews, 2008). From the Arkoma Basin through the Ozark Uplift, the depositional environment transitioned from marine shelf conditions into a very shallow carbonate ramp and tidal flat. In northwestern Arkansas a fluvial depositional environment prevailed during deposition of the Morrow.

Andrews (1995) mentioned that the Morrow in the Anadarko Basin shows a very complex character and does not fit into a simple depositional model. He defined the Morrow depositional system as a “Dynamic system containing several different, but spatially interactive environments”. The main reason for that is the frequent sea level changes that significantly influenced the position of the shoreline and caused discontinuous sandstone bodies to be deposited under highly dynamic conditions (Bowen and Weimer, 2003). Periodic sea level changes also caused sediments from different depositional environments to be found in very close proximity to each other due to sediment shifting in response to sea level change. Thus, sea level fluctuations combined with periodic sediment influx formed erratic sandstone bodies that vary in thickness, lateral extent and depositional origin, and are embedded in fine marine clastic (Bowen and Weimer, 2003).

The depositional history of the Lower Morrow Formation in the Western Oklahoma portion of the Anadarko Basin is mainly associated with shallow marine conditions. The Lower Morrow is characterized as a marine shale with interbedded discontinuous sandstone bodies (Higley et al., 2014). Andrews (1995) suggested that some localized areas in the basin show a stratigraphic transition in depositional

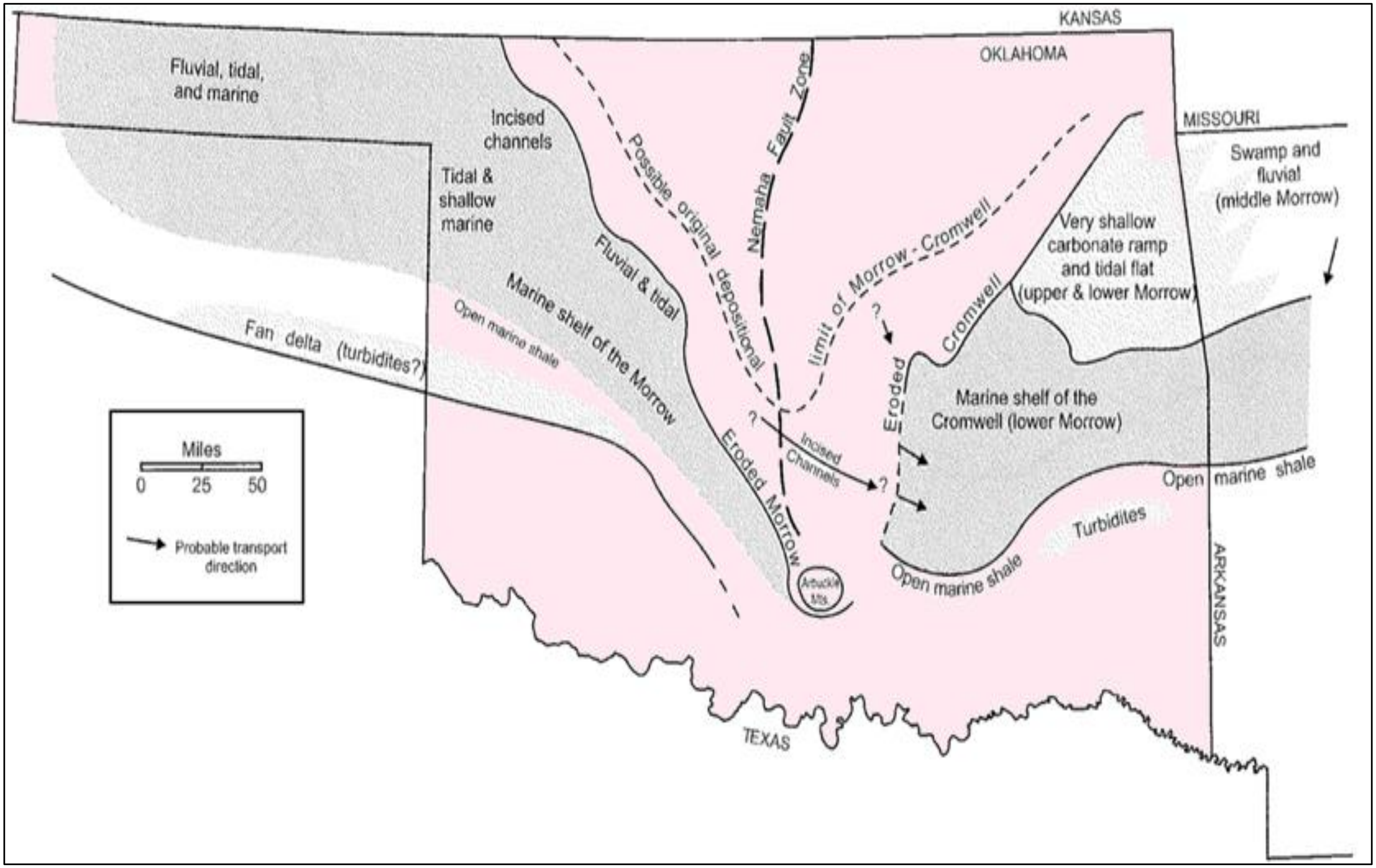


Figure 7. Paleogeographic Map Showing Reconstruction of the Morrow Formation in Oklahoma (Andrews, 2008)

environment from marine to subaerial depositional conditions such as fluvial channels and marshes. Although geometries of the sandstone bodies are related to fluvial channels, presence of marine fossil fragments and glauconite in the fluvial bars indicate that these channels were influenced by periodic sea level fluctuations (Andrews, 1995). During relative sea level rise, fluvial systems were flooded by shallow marine water, which caused the redistribution of the fluvial sediments and deposition of discontinuous sand bodies in marine shales (Puckette et al., 1996). This observation parallels the study of Buatois et al. (2002) who suggested that the Lower Morrow was deposited in a wave-dominated estuarine setting in Western Kansas (Figure 8). The Upper Morrow Formation in the Anadarko Basin is mainly characterized with shallow marine fine clastics deposited on a low gradient shelf with channel sandstones. There are different ideas about depositional environments of the Upper Morrowan clastics. Khaiwka, (1968) and Shelby (1980) claimed that the Upper Morrow sandstones are characterized by deltaic processes and Walker (1986) added that these deltas are tide-dominated. Andrews (1999) agrees with the delta scenario, however, he adds that it is not the case everywhere in Oklahoma. He suggested that there are fluvial valley fill systems in the Oklahoma Panhandle different than the deltas, which incised into the shallow marine shelf during sea level fall. In Oklahoma, sediment supply and amount of the relative sea level change were the two basic factors that controlled the occurrence of either fluvial or deltaic depositional environments. When relative sea level fell significantly, fluvial activity with incised valley channels was more dominant.

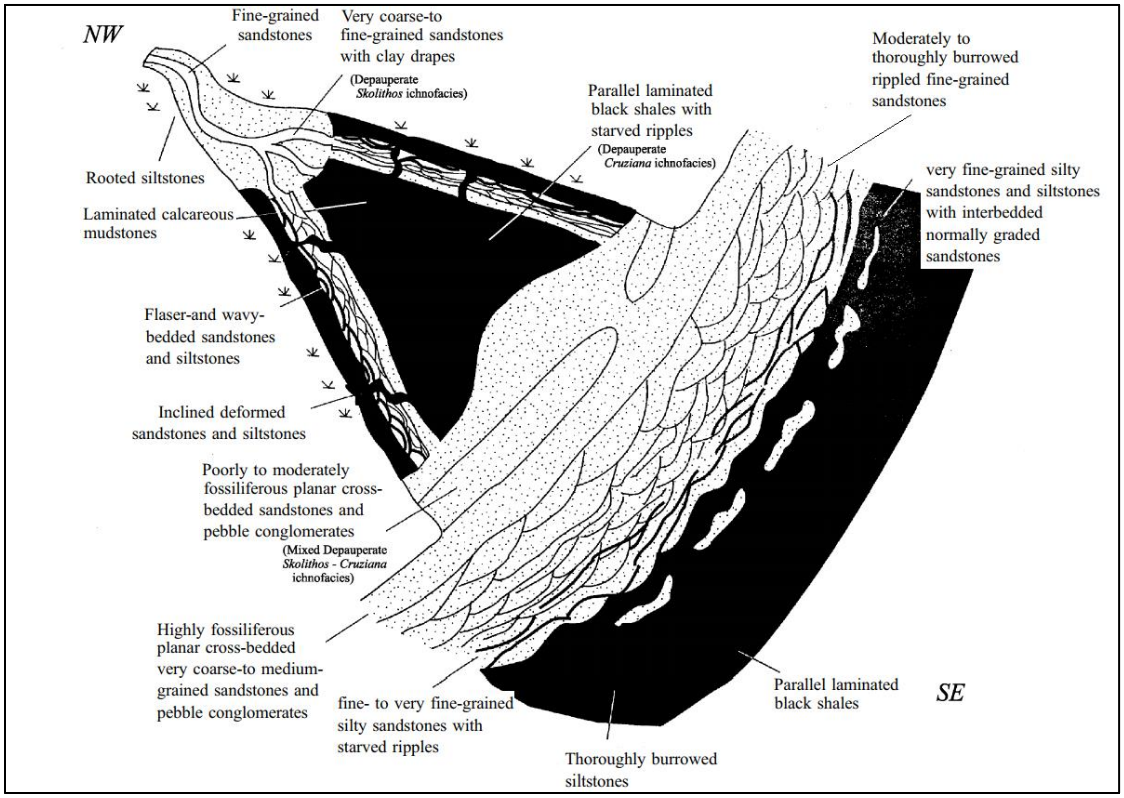


Figure 8. Depositional model for the Lower Morrow in southwest Kansas. Fluvio-estuarine valley is oriented NW – SE and displays the tripartite division (sand–mud – sand) of wave-dominated estuaries (Modified after Buatois et al., 2002)

2.5 The Morrow Formation in a Sequence Stratigraphic Framework

The Morrow Formation was deposited as a result of several transgressive and regressive cycles caused by tectonic and glacio-eustatic effects during the early Morrowan time (Al-Shaieb et al., 1995). Depositional conditions and facies distribution were mainly controlled by sea-level changes and the amount of sediment supply (Puckette et al., 2008). During lowstand periods, when sea level dropped drastically, the shelf was exposed; the fluvial channels eroded the underlying strata while extending beyond the shelf (Figure 9). This erosional surface is called the sequence boundary. During subsequent sea level rise, fluvial clastics were entrapped within the channels and inundated with shallow marine deposits dominated with mud and silt (Figure 10). When sea level rise continued

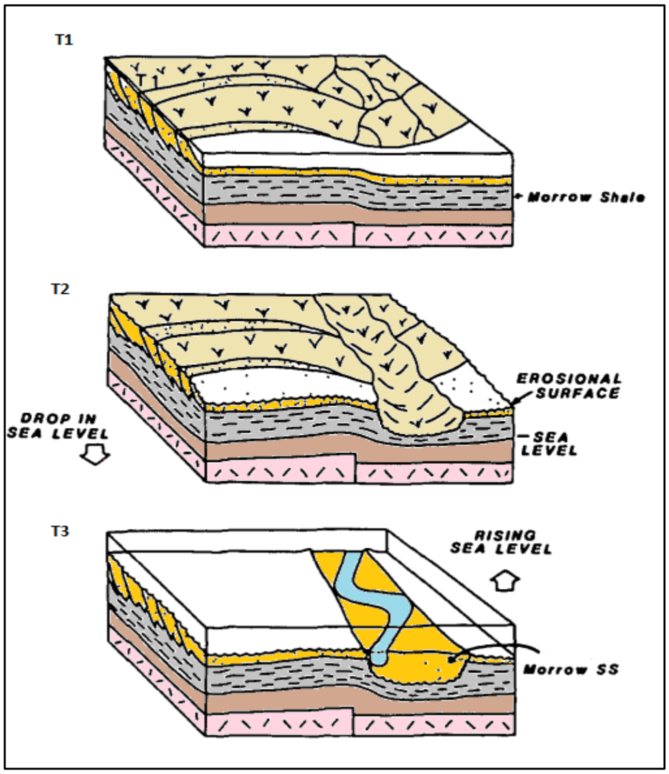


Figure 9. Block Diagram showing hypothetical clastic deposition at the Morrow Formation. T1: The Morrow Shale is deposited under thin regressive Morrow Sandstone. T2: Regional erosion surface is formed due to drop in sea level. Fluvial channels incised the underlying marine shales during sea level drop. T3: During subsequent sea level rise, valleys are filled with fluvial deposits. Marine shale deposition on the channel fill deposits (Modified from Sonnenberg, 1985).

uninterrupted, meandering or estuary deposits overlaid coarser braided river deposits which caused heterogeneity in the isolated sand bodies (Puckette et al., 2008). The maximum flooding surface was formed during the maximum flooding of the shelf and it was composed of marine organically rich fine grained sediments. This surface separated the transgressive and highstand system tracts and after its formation, the rate of sea level rise decreased with subsequent increasing sediment supply from the continent. During the highstand period, shallow marine clastics prograded and aggraded on the marine flooding surface, which was followed by another lowstand period.

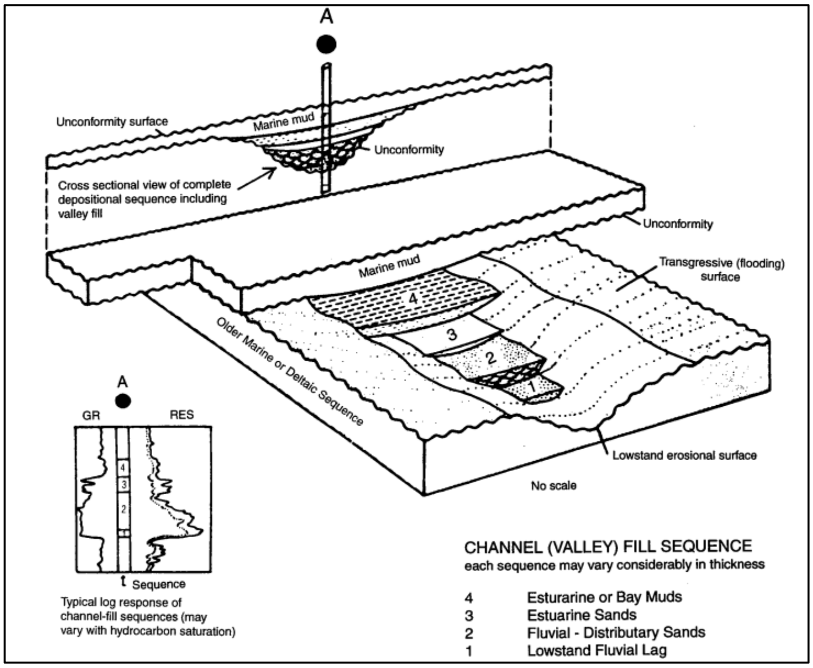


Figure 10. Schematic block diagram illustrating depositional style and vertical sequence of clastic rock facies that characterize Morrow-channel fill deposits. These channels may represent fluvial and/or distributary deposits that were affected by marine processes such as those in estuarine or tidal environments (Modified from Weimer et al., 1988).

Deposition of the Lower Morrowan sediments on the Mississippian unconformity surface started with the Pennsylvanian transgression during which various clastic sediments were deposited on the Mississippian surface under shallow marine conditions (Forgotson et al., 1966). The Lower Morrow is composed of fine grained marine clastic sediments intercalated with fluvial channel sandstones. Relative sea level continued to rise until the end of the Middle Morrowan time. During the Middle Morrowan time, the marine environment became more predominant but there was very low sediment supply and sea water temperature was suitable enough for carbonate deposition. Squaw Belly formation, which is composed of limestone and calcareous shale, has been proposed to form the boundary between the Lower and the Upper Morrow by Benton (1973), Swanson (1979) and Shelby (1980), while the other authors named this unit as the Middle Morrow Formation (Forgotson et al., 1966; Nolte, 1990; Puckette et al., 1996). During the Late Morrowan time, relative sea level fall and tectonic uplifts supplied coarse clastics which were distributed by distributary channels through the basin (Figure 11). During this period, shale was deposited in prodeltas. Fluctuations in relative sea level during the Late Morrowan time resulted in repetitive sequences of interbedded terrestrial and marine sediments of the Upper Morrow (Tsiris, 1983). The Morrowan period was followed by Atokan transgression during which the Thirteen Finger Limestone was deposited (Wheeler et al., 1990).

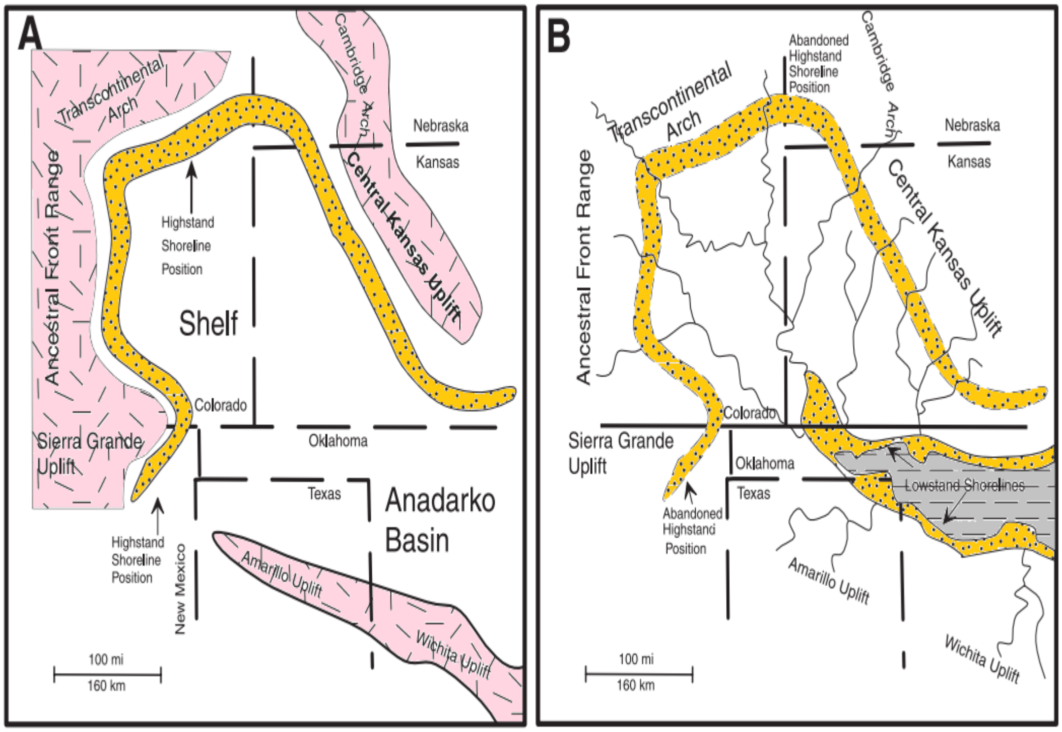


Figure 11. Schematic diagrams showing the distribution of depositional systems during deposition of the Morrow Formation. (A) During relative highstand of sea level, shorelines rimmed the basin, and black muds were deposited on a shallow widespread shelf. (B) During relative lowstand of sea level, an extensive series of drainages developed in the eastern Colorado and the western Kansas that flowed into the Anadarko basin (Modified after Bowen and Weimer, 2003)

Chapter 3: Methodology

3.1 Study Area and Sample Locations

The main purpose of this study was to define geochemical characteristics of the Morrow Shale within the Anadarko Basin. For this purpose, three sets of samples have been analyzed. The first set of 15 source rock samples were from the PhD thesis of Huai da Wang and were re-analyzed in this study (Wang, 1993). These source rock samples were collected from various depths of different wells in the Anadarko Basin, Oklahoma so that they reflect the geochemical trends in the Anadarko Basin as comprehensively as possible. These samples are referred with the “MOR” abbreviation in this study. The second set of samples used in this study belongs to the Kephart-1 Well which was drilled by Humble Oil in Blaine County, Oklahoma. The latitude and the longitude of the core is 36.0285672 and -98.4765914, respectively which corresponds to section, township and range of 20-18N-12W. In order to have high-resolution results, a total of 30 samples were collected as chips at 1 ft. intervals. The core is comprised of the Morrow Formation and was mainly black shale with alternating carbonate and siltstone layers. The Kephart-I core samples are referred with the “A” abbreviation (such as A-1, A-2 and A-3 etc.). The third set of samples was composed of two source rock samples taken from the Laverne-State-1 Well which was drilled by Gulf Oil Company in Harper County, Oklahoma. These source rock samples were gathered from two different depths of the core and collected as chips and referred with the “H” letter such as H-2 and H-3. Both core samples were obtained from the Oklahoma Petroleum Information Center (OPIC). Depth and location of the samples are given in Table 1 and shown in Figure 12.

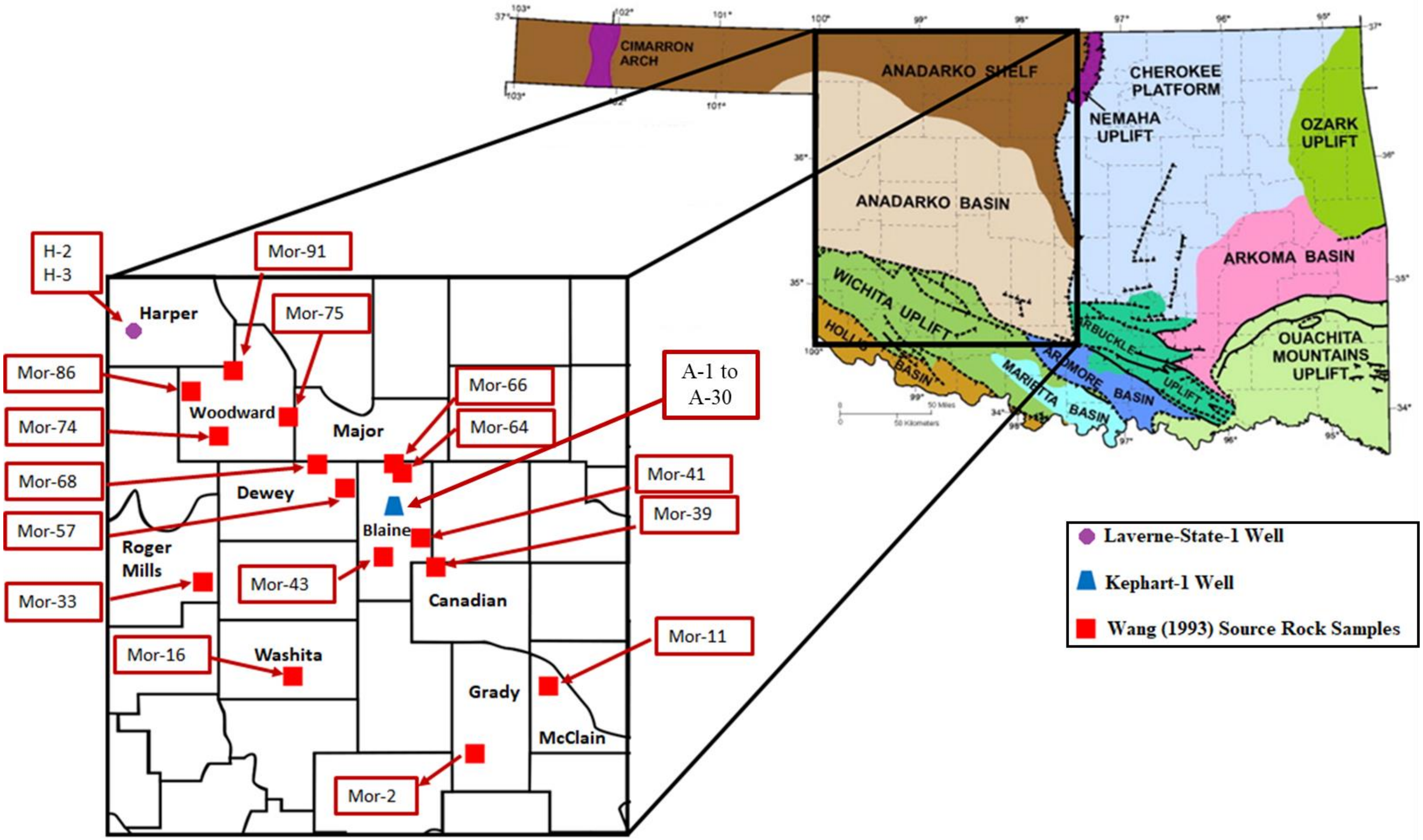


Figure 12. Location Map of the Studied Samples (Modified from Cardott, 2012)

Table 1. Sample names, depths and locations of the Morrow source rock samples

Sample Name	Depth (ft)	Township	Range	Section	County
Mor-2	13744	5N	8W	28	GRADY
Mor-11	14630	8N	5W	36	GRADY
Mor-16	16305	8N	17W	20	WASHITA
Mor-33	18909	12N	21W	3	ROGER MILLS
Mor-39	10171	14N	10W	2	CANADIAN
Mor-41	10269	15N	11W	1	BLAINE
Mor-43	10816	15N	12W	3	BLAINE
Mor-57	9077	18N	14W	2	DEWEY
Mor-64	7943	19N	12W	2	BLAINE
Mor-66	8263	19N	12W	3	BLAINE
Mor-68	8338	19N	15W	4	DEWEY
Mor-74	10395	20N	21W	3	WOODWARD
Mor-75	7899	21N	17W	1	WOODWARD
Mor-86	9154	23N	22W	3	WOODWARD
Mor-91	7466	24N	20W	2	WOODWARD
H-2	7010	26N	25W	13	HARPER
H-3	7035	26N	25W	13	HARPER
A-1	8492	20N	18W	12	BLAINE
A-2	8493	20N	18W	12	BLAINE
A-3	8494	20N	18W	12	BLAINE
A-4	8495	20N	18W	12	BLAINE
A-5	8497	20N	18W	12	BLAINE
A-6	8500	20N	18W	12	BLAINE
A-7	8502	20N	18W	12	BLAINE
A-8	8504	20N	18W	12	BLAINE
A-9	8506	20N	18W	12	BLAINE
A-10	8508	20N	18W	12	BLAINE
A-11	8511	20N	18W	12	BLAINE
A-12	8513	20N	18W	12	BLAINE
A-13	8515	20N	18W	12	BLAINE
A-14	8517	20N	18W	12	BLAINE
A-15	8518	20N	18W	12	BLAINE
A-16	8520	20N	18W	12	BLAINE
A-17	8523	20N	18W	12	BLAINE
A-18	8524	20N	18W	12	BLAINE
A-19	8526	20N	18W	12	BLAINE
A-20	8529	20N	18W	12	BLAINE
A-21	8531	20N	18W	12	BLAINE
A-22	8532	20N	18W	12	BLAINE
A-23	8534	20N	18W	12	BLAINE
A-24	8536	20N	18W	12	BLAINE
A-25	8536.5	20N	18W	12	BLAINE
A-26	8539	20N	18W	12	BLAINE
A-27	8541	20N	18W	12	BLAINE
A-28	8545	20N	18W	12	BLAINE
A-29	8548	20N	18W	12	BLAINE
A-30	8550	20N	18W	12	BLAINE

3.2 Experimental Procedure

3.2.1 Preliminary Sample Treatment

Both of the cores were drilled many years ago and they consist of rock chips rather than a whole core or slab. The chips were rinsed thoroughly with the mixture of methanol and dichloromethane (MeOH: DCM; 1:1) in order to eliminate potential organic contaminants that might have penetrated the core. Then, they were left to air dry for about 24 hours prior to crushing.

After eliminating potential surficial contamination, each sample was crushed into small pieces with a porcelain mortar and pestle (Figure 13). Then a maximum of 8 grams of sample and several steel balls were introduced into a cylindrical vessel and sealed with a cap. Then the sealed vessel was fixed into a Spex 8000 Mixer/Mill and crushed into a fine powder for about 4 minutes depending on its clay/carbonate content. This process was run through several times until the desired amount of 50 grams of fine powder with grain size smaller than 0.425 mm (US Standard mesh No. 40) were collected.

Figure 13. Laboratory Equipments Used for Rock Crushing

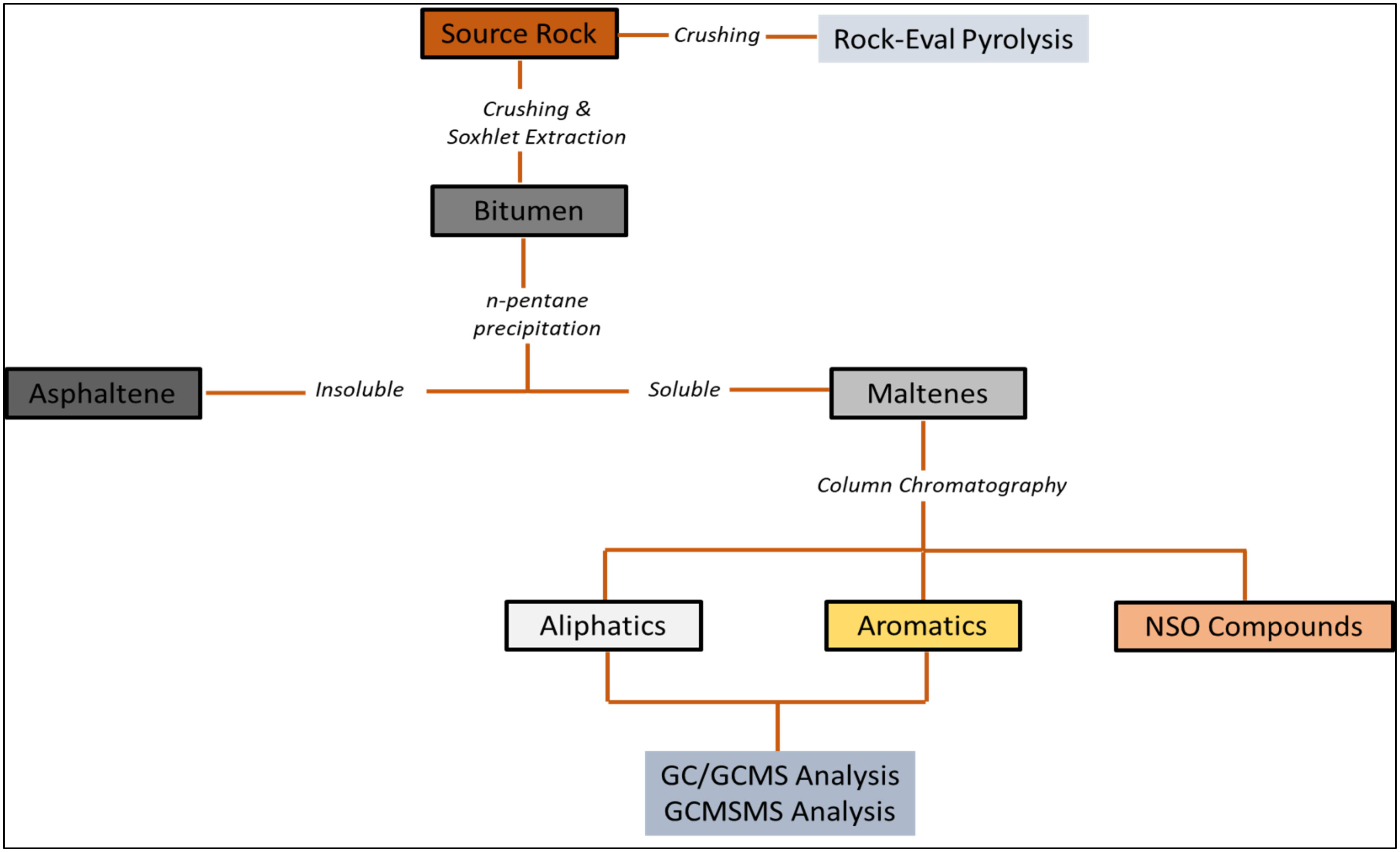


Figure 14. Sample Preparation Flowchart

3.2.2 Rock Eval Pyrolysis

Organic matter characterization is crucial for interpreting the geology and petroleum generation potential of any source rock (Langford and Blanc-Valleron, 1990). Rock-Eval pyrolysis is a source rock screening technique that provides valuable information about quantity, type and thermal maturity of the organic matter (OM) within the source rock (Peters, 1986; Peters and Cassa, 1994). It is a commonly used method as it is practical, inexpensive and requires only small amounts of samples (100 mg) to provide geochemical data (Sykes and Snowdon, 2002).

The Rock-Eval instrument basically heats finely crushed rock samples at a programmed temperature rate in the absence of oxygen (Peters, 1986; Sykes and Snowdon, 2002). During the pyrolysis, the temperature of the oven is kept at 300°C for 3 minutes. Organic compounds produced during pyrolysis are detected by a flame ionization detector (FID). Free hydrocarbons already present in the sample, both free and occluded, are first volatilized and then detected by the FID as the S_1 peak. The S_1 peak represents the free hydrocarbons already present in the source rock. The temperature is then increased from 300°C to 550°C at 25°C/min. Thermal degradation of the kerogen produces hydrocarbons which are represented by the S_2 peak, and organic oxygen as CO_2 derived from kerogen decomposition represented by the S_3 (Figure 15). The S_2 peak illustrates the potential generative capacity of a source rock and is measured in milligrams of hydrocarbon per gram of rock (mg HC/ g rock; Tissot and Welte, 1984. The S_3 peak is used to calculate organic oxygen in the kerogen fraction of the sample and is represented as mg of carbon dioxide per gram of rock (mg CO_2 / g rock; Peters, 1986). The S_4 peak corresponds to the residual organic carbon after pyrolysis, which is unable to generate additional hydrocarbons. As maturity of the source rock increases, the S_1 peak and the S_4

peak increases but intensity of the S_2 peak decreases due to remaining generative capacity of the rock diminishing (Peters, 1986). The total organic carbon (TOC) of the rock is determined as weight percent (wt. %) of the whole rock and calculated by adding the pyrolyzed and residual carbon amounts to each other. The T_{max} value corresponds to the highest point of the S_2 peak and is used to evaluate the maturity level of the sample. The hydrogen index (HI) is calculated by S_2 (mg HC/g rock) / TOC (wt. %), the oxygen index (OI) is calculated as S_3 (mg CO_2/g rock)/TOC (wt. %) while the production index (PI) is calculated by $S_1 / (S_1 + S_2)$.

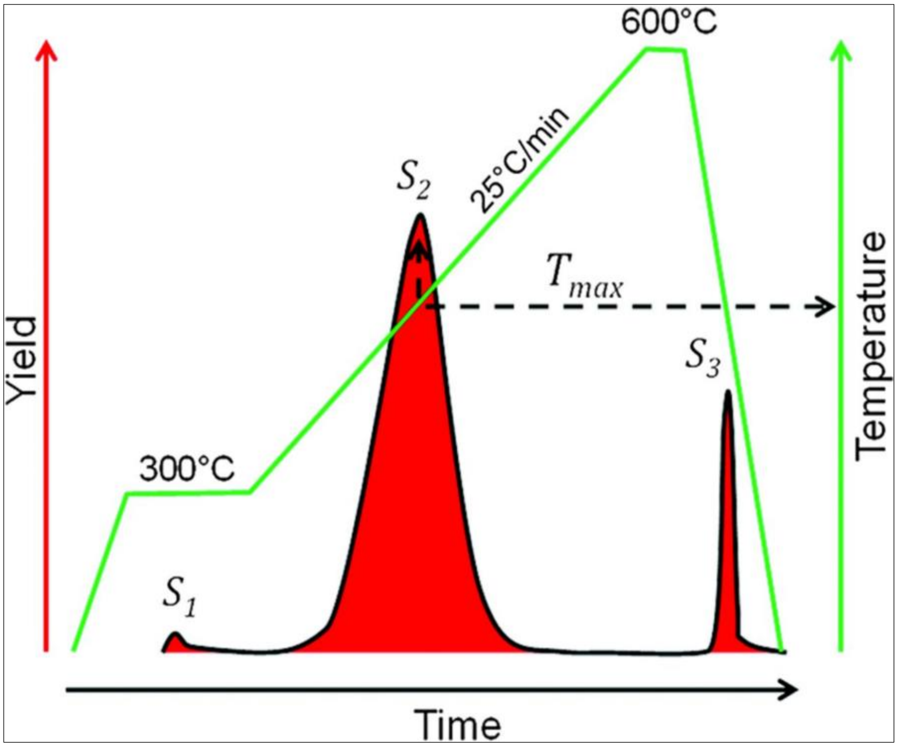


Figure 15. Simplified pyrogram profile of a traditional Rock-Eval Method (Hart and Steen, 2015)

Kerogen is classified using a pseudo van Krevelen diagram which was first proposed by van Krevelen in 1950. van Krevelen constructed this model based on hydrogen and oxygen abundances of coal relative to carbon (Figure 16; van Krevelen, 1950). The diagram was immediately accepted by the geochemistry community in early years and has been widely used as a tool for kerogen classification for a long time.

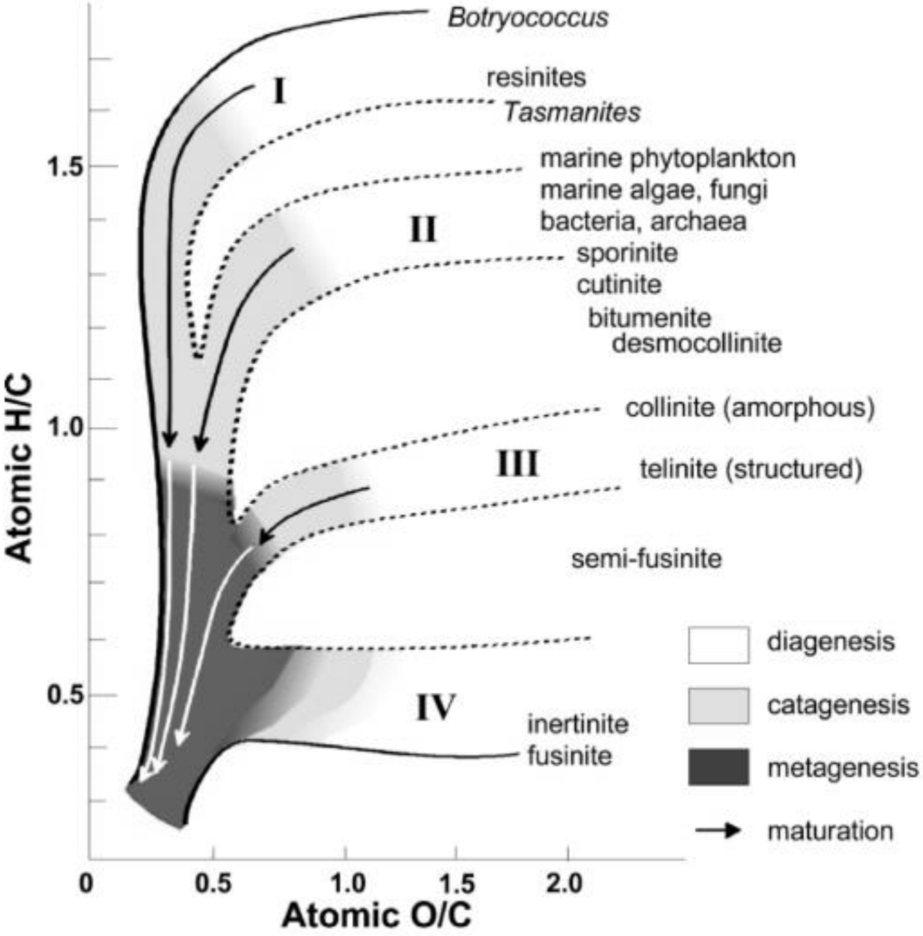


Figure 16. van Krevelen type diagram showing the distribution of kerogen types and some of their precursor macerals in relationship to their H/C and O/C atomic ratios (Walters, 2007)

In the petroleum geochemistry, the van Krevelen plot is mainly used for determining the type of organic matter and the type of hydrocarbons produced. Espitalié et al. (1977) integrated pyrolysis indices into the van Krevelen Diagram and proposed a new pseudo-van Krevelen diagram (PVK). However, Baskin (1979) suggested that the pseudo-van Krevelen is not as efficient as the original diagram in terms of assessing organic matter quality and maturity as it was initially proposed for integration of atomic ratios rather than pyrolysis data. Moreover, PVK has some limitations when characterizing rocks with low TOC and type-III kerogen with high TOC. Thus, these conflicts should be considered when the kerogen types are identified with use of PVK integrated with Rock-Eval data. Nevertheless, in today's exploration efforts, the modern PVK diagram is widely used for kerogen characterization by means of HI and OI ratios. PVK separates four kerogen types as Type I (oil prone-generally lacustrine); Type II (oil prone-marine); Type III (gas prone) and Type IV (inert). Waples (1985) mentioned that kerogen type in the sediments determines its generative capacity. For instance, Type-I kerogen is composed of hydrogen-rich and oxygen-lean organic matter that is more prone to produce oil and has more remaining generative capacity. Moreover, HI values below 150 mg/g are indicative of Type-III kerogen with gas generative capacity. Samples with HI values between 150-300 mg/g have a mixed type of organic matter and can generate both oil and gas. HI values above 300 mg/g can be characterized as Type-II and they are a good source for oil generation. Samples with HI values above 600 mg/g are mainly characterized as Type I/II kerogen; which are excellent sources for oil production (Waples, 1985).

The source rock samples of Wang (1993) had been previously characterized by a Rock-Eval type instruments called RUSKA PYRAN Level I-FID System. It is now an outdated instrument and has not been used by the petroleum sector for a long time. Although RUSKA PYRAN and the traditional Rock-Eval instrument shared common working principles, they have different temperature settings (Wang, 1993). While S_2 results of these two instruments are almost equal; the S_1 values show slight differences (Wang, 1993). Also, the T_{max} results of these instruments are very different (Wang, 1993).

Thus, in this study, S_1 and S_2 results were used as they were but T_{max} values were converted to Rock-Eval T_{max} by using the proposed conversion chart of Wang (1993) in order to plot them in pseudo-van Krevelen Diagrams. The PYRAN Level-I system did not have a thermal conductivity detector (TDC) so it was not able to detect CO_2 and produce a S_3 peak. Thus, there are no oxygen index values for the source rock samples in Wang's (1993) thesis. The rock samples from Wang (1993) were no longer available and hence could not be reanalyzed. The core samples, however, were crushed into 40-mesh size and approximately 1 g of each sample were sent to the GeoMark Research Company in Humble, Texas for Rock-Eval and total organic carbon analysis.

3.2.3 Soxhlet Extraction

A Soxhlet extraction system was used to extract soluble organic matter from the rock samples. First, all of the components (thimble, glass wool, flask, and condenser) in the Soxhlet system were pre-extracted with a mixture of DCM and MeOH (250 mL:250 mL) for 24 hours in order to eliminate potential contamination risk. After 24 hours the crushed and weighed rock samples were introduced carefully into the cellulose thimbles and then installed in the Soxhlet system together with fresh solvent. Finally, each sample was extracted for 48 hours under moderate temperature conditions and the extracted resulting bitumen collected in a round bottom flask.

The solvent was removed from the bitumen extract using a rotary evaporator. The extract was diluted with a small amount of DCM, then passed through a packed glass wool in order to filter any dissolved particles and collected in pre-weighed 20 ml vials. Finally, the mixture was dried by using Organomation Model 112 Analytical Evaporator under moderate nitrogen flow and the bitumen extract was weighed.

3.2.4 Deasphalting of the Bitumen

Extracted organic matter (bitumen) is composed of an asphaltene and maltene fraction that can be separated by precipitation with pentane or hexane. Maltenes have lower average molecular weights than asphaltenes and are soluble in pentane or hexane whereas the asphaltenes are insoluble. In order to deasphaltene the bitumen, 200 mg of sample, which was diluted with a minimum amount of DCM, was introduced in a centrifuge tube. Then, the tube was partially submerged into a Branson 2510 Model sonicator filled with deionized water. After that, the sonicator was turned on and n-pentane was added drop by drop into the centrifuge tube until the solvent amount reached the shoulder of the tube. Then, it was put in a freezer for overnight to allow a decent time for deasphalting. The tubes were subsequently centrifuged 10 minutes by using a Damon IEC Model centrifuge in order to settle suspended asphaltene particles. The dissolved maltene fraction was then transferred into a 250 ml flask and solvent was removed by the rotary evaporation. Finally, the resultant maltene fraction was transferred into 2 ml vials with a minimum amount of DCM, subjected to evaporation using nitrogen until all the solvent was removed, then weighed. The results are presented in Table 2.

3.2.5 Maltene Fractionation: Column Chromatography

Column chromatography was used to fractionate the maltenes into aliphatic, aromatic and polar fractions in this study. The method was designed and verified by Dr. Thanh X. Nguyen. A silica column was packed in a 5 3/4” Pasteur-type pipettes. First, glass wool, which was used as filter, was placed at the bottom of the pipette. Then, 3.8 g of silica, which was heated at 120^0C for at least 12 hours, was gradually added on glass wool. Hexane was used to pack the column and air was used to push the hexane through

Table 2. Sample weights of extract, asphaltene, maltene, and the resulting yields of each sample. (Note that the data belonging to Wang (1993) below are taken directly from his thesis to show the general character of the Morrow Shale; percentages are of the total maltene fractioned.)

Sample ID	Maltene (mg)	Aliphatics(mg)	Aromatics(mg)	NSO(mg)	% Aliphatics	% Aromatics	% NSO
Mor-2	91.80	6.86	3.09	9.55	35.18	15.85	48.97
Mor-11	90.50	2.64	1.92	4.00	30.84	22.43	46.73
Mor-16	91.30	25.40	2.21	5.50	76.71	6.67	16.61
Mor-33	102.80	9.23	2.53	2.78	63.48	17.40	19.12
Mor-39	100.40	6.52	2.28	5.34	46.11	16.12	37.77
Mor-41	81.90	4.20	1.85	5.23	37.23	16.40	46.37
Mor-43	106.70	3.12	2.31	13.15	16.79	12.43	70.78
Mor-57	70.40	6.85	5.87	14.36	25.30	21.68	53.03
Mor-64	92.40	26.18	5.42	20.27	50.47	10.45	39.08
Mor-66	90.10	26.65	7.25	17.88	51.47	14.00	34.53
Mor-68	90.80	16.83	4.03	9.12	56.14	13.44	30.42
Mor-74	103.40	3.82	3.68	7.14	26.09	25.14	48.77
Mor-75	100.20	3.75	6.06	8.57	20.40	32.97	46.63
Mor-86	90.40	10.44	2.05	9.89	46.65	9.16	44.19
Mor-91	111.00	8.88	5.43	13.15	32.34	19.77	47.89
A-1	96.15	5.95	4.73	2.40	45.49	36.16	18.35
A-2	30.89	10.65	1.03	1.79	79.06	7.65	13.29
A-3	139.82	10.56	1.35	0.73	83.54	10.68	5.78
A-4	118.63	9.26	1.51	1.05	78.34	12.77	8.88
A-5	219.62	10.76	1.63	0.55	83.15	12.60	4.25
A-6	229.40	11.88	2.27	0.86	79.15	15.12	5.73
A-7	184.18	13.56	1.79	1.20	81.93	10.82	7.25
A-8	270.11	10.86	1.79	2.28	72.74	11.99	15.27
A-9	103.27	11.02	2.97	1.66	70.42	18.98	10.61
A-10	87.74	7.98	2.53	0.85	70.25	22.27	7.48
A-11	53.20	12.11	2.52	2.32	71.45	14.87	13.69
A-12	49.43	8.73	3.28	2.49	60.21	22.62	17.17
A-13	78.61	8.20	2.05	1.26	71.24	17.81	10.95
A-14	34.03	7.96	3.26	1.47	62.73	25.69	11.58
A-15	45.75	6.94	2.42	0.42	70.96	24.74	4.29
A-16	39.74	6.68	2.28	1.86	61.74	21.07	17.19
A-17	30.80	6.79	3.69	2.46	52.47	28.52	19.01
A-18	33.75	6.51	2.89	2.68	53.89	23.92	22.19
A-19	29.95	2.18	2.53	0.92	38.72	44.94	16.34
A-20	47.50	6.45	1.81	0.55	73.21	20.54	6.24
A-21	38.07	6.12	1.26	0.79	74.91	15.42	9.67
A-22	24.42	4.42	2.70	1.33	52.31	31.95	15.74
A-23	41.35	2.82	2.65	1.84	38.58	36.25	25.17
A-24	32.80	7.48	2.00	1.30	69.39	18.55	12.06
A-25	20.91	6.78	2.95	1.29	61.52	26.77	11.71
A-26	43.32	5.62	2.44	1.18	60.82	26.41	12.77
A-27	37.35	4.80	2.80	1.95	50.26	29.32	20.42
A-28	22.45	4.98	2.45	1.15	58.04	28.55	13.40
A-29	116.79	6.08	1.80	1.08	67.86	20.09	12.05
A-30	64.15	10.23	2.27	4.10	61.63	13.67	24.70
H-2	78.54	1.33	2.86	1.24	24.49	52.67	22.84
H-3	14.59	4.56	2.33	2.29	49.67	25.38	24.95

the column and to displace any bubbles. Maltene (17.5 mg) was dissolved in 200 µl hexane and introduced carefully on the top the silica and was allowed to drain completely through the column. Hexane (8.5 ml) was added to the column without disturbing the silica and passed through the column to elute the aliphatic compounds in 100 ml flask. Then 25 ml of hexane:DCM mixture (v/v=7:3) was added to the column and the aromatic fractions eluted in a 100 ml flask. Finally, 25 ml of CHCl3:MeOH mixture (v/v=98:2) was added to the column and drained to collect polar compounds in a 100 ml flask. Excess amounts of solvent were removed from the flasks using rotary evaporation and the fractions were transferred into 4ml vials, which were already weighed using minimum amounts of DCM. Solvent was evaporated under a stream of nitrogen and the vials were reweighed. The fraction masses are given in Table 2.

3.2.6 Gas Chromatography

Aliphatic and aromatic fractions were screened by gas chromatography using an Agilent Technologies 6890 Gas Chromatograph (GC). The samples were diluted to 5 mg/ml in hexane and were injected using a splitless injection method onto the column. Helium was used as carrier gas with a flow rate of 1.4 ml/min. The fused silica capillary column was a 60 m long DB-5MS model silica column with 0.32 mm inner diameter and 0.032 mm thick coating. The method was set up with an initial temperature of 40^{O}C for 1.5 minutes after the injection, programmed to 300^{O}C at a rate of 4^{O}C/min and held isothermal for 24 minutes for a complete run time of 90.5 minutes.

3.2.7 Gas Chromatography-Mass Spectrometry

Aliphatic and aromatic biomarkers were determined using an Agilent Technologies 7890A gas chromatograph combined with an Agilent Technologies 5975 XL mass selective detector (MSD). The samples were diluted to 5 mg/ml in hexane and were injected with splitless injection method onto the column. A J&W Scientific DB-5MS 122-5562 fused silica column with 0.25 mm inner diameter and 0.025 mm coating was used for the gas chromatography. Flow rate of the carrier gas was 1.4 ml /min for the GC. The ionization energy of the MSD was 70 eV with an ion source temperature of 250 ^{O}C and the temperature of the quadrapole analyzer was 200^{O}C. The temperature of the program was initially set to 40^{O}C for 1.5 minutes and then increased to 300^{O}C at 4 ^{O}C/min and held isothermal for 34 minutes for a total run time of 100.5 minutes. The fractions were analyzed by both single ion monitoring (SIM) and multiple ion detection (MID) modes depending on the target compound.

3.2.8 Gas Chromatography-Mass Spectrometry-Mass Spectrometry

Gas Chromatography-Mass Spectrometry-Mass Spectrometry (GCMS-MS) was used for aliphatic and saturate compounds that were problematic to identify. A Thermo Scientific Trace 1310 gas chromatograph paired with TSQ 8000 triple quadrapole mass spectrometer and used in a splitless injection mode to analyze samples. The same dilution (5 ml/mg) used for GC and GCMS was also used for the GCMS-MS. A J&W Scientific DB-5MS 122-5562 fused silica column with 0.25 mm inner diameter and 0.025 mm thick liquid film coating was used for the gas chromatography. Helium with 1.4 ml/min flow rate was used as carrier gas and Argon was used as collision gas. The initial temperature program of the GC was set at 40^{O}C for 1.5 minutes then increased to 300^{O}C with 4 ^{O}C/min and held isothermal for 34 minutes for total run time of 100.5 minutes.

Chapter 4: Results and Discussion

4.1 Source Rock Characterization

Source rock characteristics are based on bulk geochemical data such as total carbon content, thermal maturity and kerogen type. These data are commonly obtained from the Rock-Eval pyrolysis, a standard procedure in the petroleum exploration industry. In this study, the rock samples from Kephart-1 Well and Laverne-State-1 Well were screened by Rock-Eval pyrolysis for the source rock characterization and the generated data are presented in Table 3. RUSKA PYRAN analyses data of the Wang (1993) source rock samples are given in Table 4. TOC and HI values of the samples were used to construct TOC and HI map of the Morrow Formation in the Anadarko basin (Figures 17 and 18).The maps can be used to provide additional information about the lateral changes in TOC and remaining generative potential of the Morrow Shale in the Anadarko Basin.

When evaluating Rock-Eval pyrolysis results several factors should be considered. For instance, high S_1 results can be indicative of contamination from drilling fluid additives. Non-indigenous hydrocarbons that were expelled and migrated from another source rock can also elevate the S_1 peak. Smith (1994) suggested that S_1/TOC values exceeding 1.5 indicate contribution from non-indigenous oil. Thus, in this study Rock-Eval results of the Kephart-I core samples A-4, A-6, A-7, A-8 and A-9 were considered as unreliable and rejected from the pyrolysis data.

Table 3. Rock-Eval Pyrolysis Results of the Kephart-I and Laverne-State-I Well Samples (Note that the lines that are marked with green point-out the samples that were ejected from screening and the lines that are marked with orange point-out the samples whose Tmax values were omitted.)

Samples	Depth (ft.)	Tmax (^{0}C)	TOC (wt. %)	S_1 (mg HC/ g)	S_2 (mg HC/ g)	S_3 (mg CO_2/ g)	HI (S_2 *100) / TOC	OI (S_3 *100) / TOC	PI (S_1/ S_1 + S_2)	Percent Carbonate (wt. %)	RHP (S_1 + S_2 / TOC)	Calculated% R_0	S_1 /TOC
A-1	8492.0	444	2.63	0.93	1.40	0.36	53	14	0.40	4.46	0.89	0.83	0.35
A-2	8493.0	335	0.32	0.23	0.26	0.23	81	72	0.47	4.36	1.53	-1.13	0.72
A-3	8494.0	301	0.29	0.32	0.33	0.34	114	118	0.49	4.36	2.25	-1.74	1.11
A-4	8495.0	255	0.47	1.89	0.27	0.55	57	117	0.88	9.42	4.58	-2.57	4.00
A-5	8497.0	310	1.35	0.92	0.54	0.32	40	24	0.63	5.93	1.08	-1.58	0.68
A-6	8500.0	417	0.94	4.41	1.23	0.27	131	29	0.78	14.41	6.01	0.35	4.70
A-7	8502.0	447	1.38	3.66	2.11	0.16	153	12	0.63	8.16	4.18	0.89	2.65
A-8	8504.0	433	1.72	3.17	1.88	0.45	109	26	0.63	20.21	2.94	0.63	1.84
A-9	8506.0	450	3.02	4.56	3.37	0.94	112	31	0.58	55.21	2.63	0.94	1.51
A-10	8508.0	436	1.09	0.90	0.80	0.46	73	42	0.53	33.97	1.56	0.69	0.83
A-11	8511.0	443	1.14	0.65	0.36	0.42	32	37	0.64	6.16	0.89	0.81	0.57
A-12	8513.0	451	0.37	0.40	0.21	0.30	57	81	0.66	4.52	1.65	0.96	1.08
A-13	8515.0	451	1.44	0.49	0.89	0.29	62	20	0.36	3.70	0.96	0.96	0.34
A-14	8516.5	455	1.27	0.45	0.67	0.32	53	25	0.40	7.81	0.88	1.03	0.35
A-15	8518.0	456	1.13	0.22	0.51	0.32	45	28	0.30	8.53	0.65	1.05	0.19
A-16	8520.0	458	0.56	0.33	0.59	0.25	105	45	0.36	2.58	1.64	1.08	0.59
A-17	8523.0	461	1.47	0.26	0.64	0.34	44	23	0.29	4.64	0.61	1.14	0.18
A-18	8523.5	459	1.38	0.22	0.52	0.48	38	35	0.30	10.52	0.54	1.10	0.16
A-19	8526.0	463	1.30	0.18	0.58	0.55	45	42	0.24	19.46	0.58	1.17	0.14
A-20	8529.0	460	1.79	0.30	0.80	0.54	45	30	0.27	8.35	0.61	1.12	0.17
A-21	8531.0	458	1.71	0.33	0.80	0.47	47	27	0.29	4.97	0.66	1.08	0.19
A-22	8532.0	455	2.85	0.36	0.94	0.45	33	16	0.28	6.18	0.46	1.03	0.13
A-23	8534.0	465	0.59	0.23	0.21	0.69	36	117	0.52	8.90	0.75	1.21	0.39
A-24	8536.0	452	0.60	0.16	0.23	0.16	38	27	0.41	12.03	0.65	0.98	0.27
A-25	8536.5	458	1.01	0.18	0.51	0.42	50	42	0.26	19.27	0.68	1.08	0.18
A-26	8539.0	457	1.57	0.35	0.96	0.68	61	43	0.27	27.25	0.83	1.07	0.22
A-27	8541.0	452	1.90	0.43	1.27	0.20	67	11	0.25	18.94	0.89	0.98	0.23
A-28	8544.5	457	1.16	0.19	0.55	0.43	47	37	0.26	7.63	0.64	1.07	0.16
A-29	8548.0	452	1.84	0.97	2.95	0.33	160	18	0.25	21.67	2.13	0.98	0.53
A-30	8550.0	443	1.19	0.51	1.48	0.26	124	22	0.26	32.93	1.67	0.81	0.43
H-2	7010.0	433	19.60	7.14	111.72	4.58	570	23	0.06	53.29	6.06	0.63	0.36
H-3	7035.0	438	6.30	0.88	2.06	0.71	33	11	0.30	15.82	0.47	0.72	0.14

Table 4. Rock-Eval pyrolysis data of the Wang (1993) source rock samples (Note that the lines that are marked with orange point-out the samples whose Tmax values were omitted due to the previously discussed reasons)

Samples	Depth (ft.)	Tmax (°C)	TOC (wt. %)	S_1 (mg HC/ g)	S_2 (mg HC/ g)	HI (S_2*100) / TOC	PI (S_1/ S_1+ S_2)	RHP (S_1 + S_2 / TOC)	Calculated % R_0	S_1/TOC
Mor-2	13744	450	1.61	0.24	0.57	36	0.30	0.50	0.95	0.15
Mor-11	14630	448	1.38	0.10	0.55	40	0.15	0.47	0.90	0.07
Mor-16	16305	486	1.59	0.10	0.40	25	0.20	0.31	1.59	0.06
Mor-33	18909	-	1.40	0.19	0.10	7	0.66	0.21	-	0.14
Mor-39	10171	453	1.42	0.10	0.67	47	0.13	0.54	1.00	0.07
Mor-41	10269	455	1.30	0.18	0.64	49	0.22	0.63	1.02	0.14
Mor-43	10816	456	1.79	0.14	0.55	31	0.20	0.39	1.05	0.08
Mor-57	9077	429	1.47	0.61	1.93	132	0.24	1.73	0.56	0.41
Mor-64	7943	422	1.52	0.87	1.86	122	0.32	1.80	0.44	0.57
Mor-66	8263	427	2.04	0.64	2.49	122	0.20	1.53	0.53	0.31
Mor-68	8338	426	1.30	0.66	2.02	155	0.25	2.06	0.51	0.51
Mor-74	10395	441	2.53	0.14	0.79	31	0.15	0.37	0.78	0.06
Mor-75	7899	428	0.99	0.12	0.75	75	0.14	0.88	0.54	0.12
Mor-86	9154	436	1.32	0.08	0.38	29	0.17	0.35	0.70	0.06
Mor-91	7466	427	1.54	0.28	0.98	64	0.22	0.82	0.53	0.18

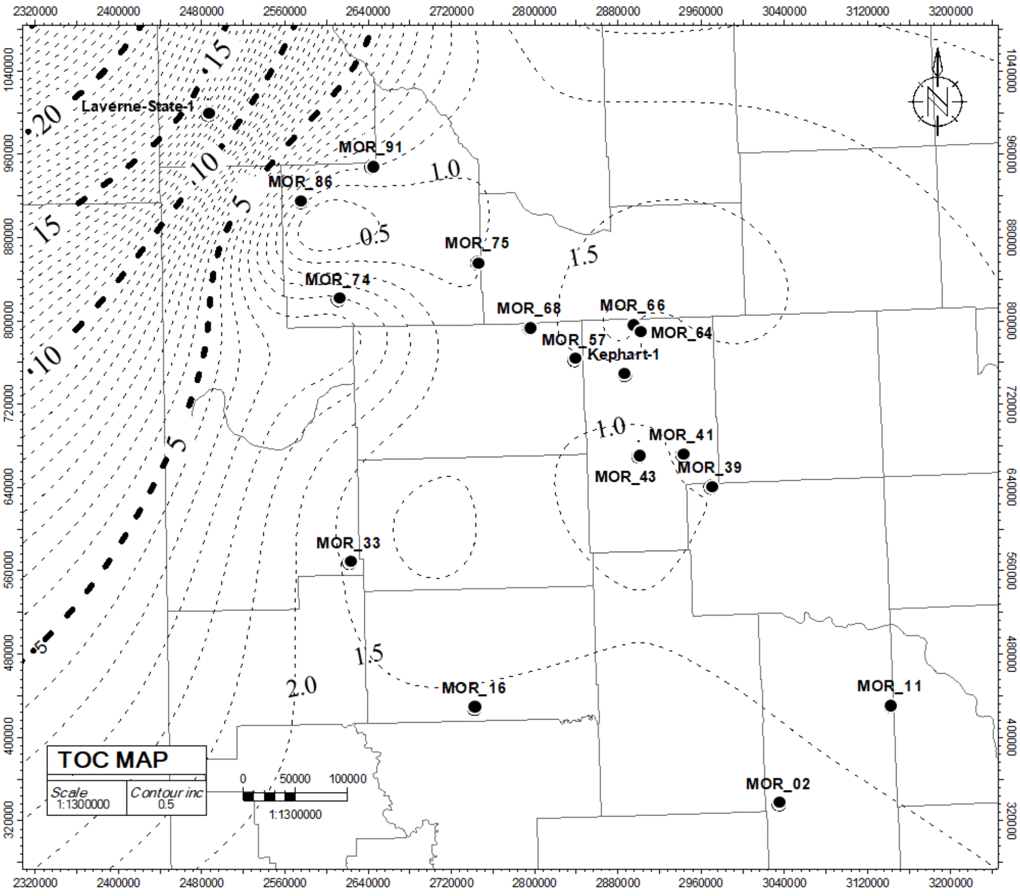


Figure 17. TOC map constructed for the study area

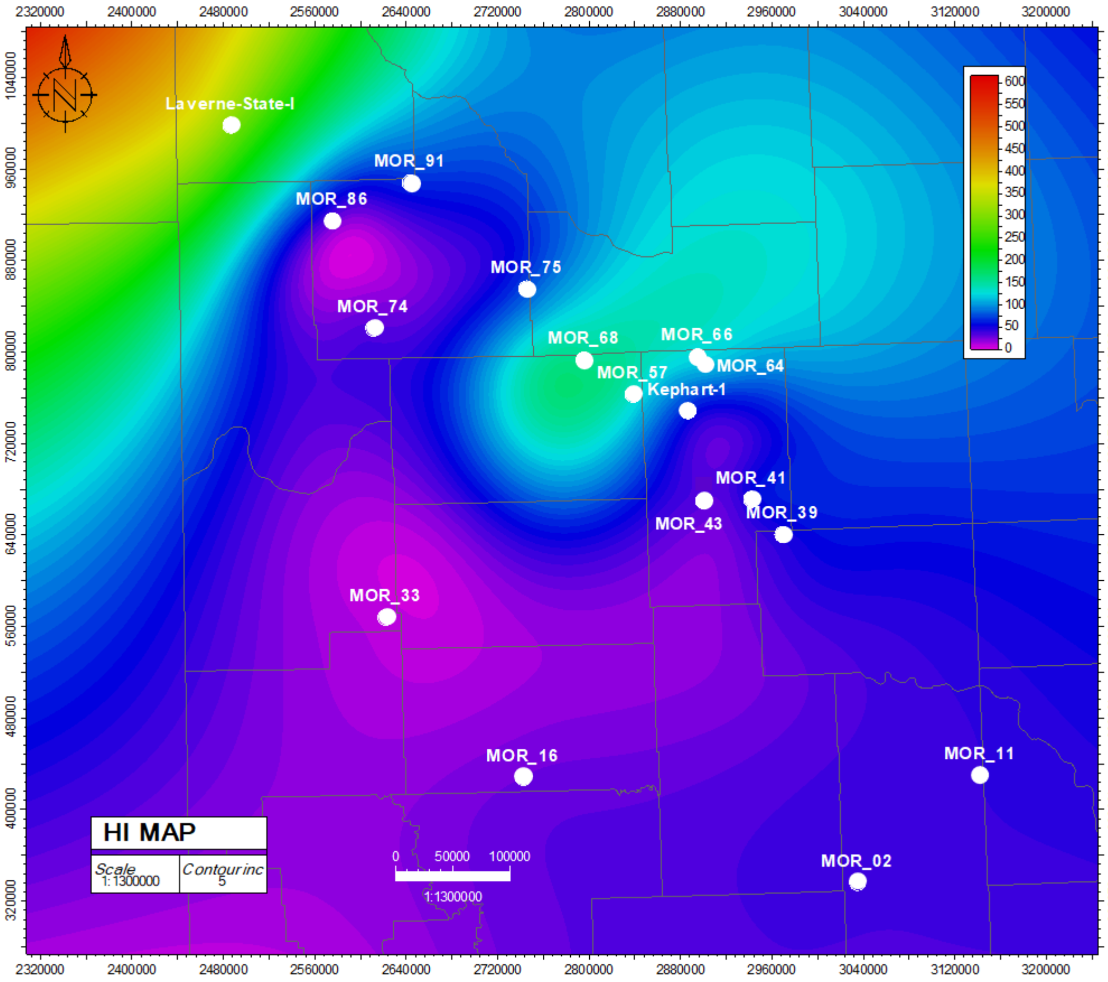


Figure 18. Hydrogen Index Map Constructed for the Study Area

The H/C atomic ratio decreases with the weathering of the source rock which will result in a reduced S_2 peak (van Krevelen, 1984). In this study, T_{max} values of the samples were ignored if their S_2 value is less than 0.5 mg HC/g rock. It's because of the fact that when the S_2 peak is too low, the peak does not appear very clear as it becomes very broad and flat instead. Although, T_{max} values can range from 300°C to 590°C (Figure 15), T_{max} values below 400°C are generally considered as anomalous if the PI of the sample is above 0.2. This condition can be related to heavy hydrocarbon staining (Nuccio and

Barker, 1989) and these samples should be treated with caution until the extract data has been examined in detail to evaluate whether contamination is present. The Tmax value of the samples that were rejected in this study and the summary of the screening parameters are given in Table 5.

Table 5. Rock-Eval Screening Parameters used for evaluation of the data

Condition	Action	The samples that were rejected
S_1/TOC > 1.5	Pyrolysis data of the sample ignored	A-4, A-6, A-7, A-8, A-9
$S_2 < 0.5$ (mg HC/g)	Ignore T_{max}	A-2, A-3, A-5, A-11, A-12, A-23, A-24, MOR-16,MOR-33,MOR-86
$T_{max} < 400\ ^{O}C$ and PI > 0.2		

4.1.1. Total Organic Content

Total Organic Carbon (TOC) is the measure of organic richness which describes the quantity of the organic matter in a source rock comprising both bitumen and kerogen (Peters and Cassa, 1994). It is represented by the weight percent of the organic matter relative to the total weight of the rock. Generally, source rocks are classified as poor if TOC values are less than 0.5 %; as fair if TOC values are in between 0.5 %-1 %; as good if TOC values range between 1%-2% ; and as excellent source rock if TOC values are more than 4% (Peters, 1986; Al-Atta et al., 2014). The TOC content of the 15 source rock samples from the Wang (1993) study range between 0.99 %- 2.53 % with average of 1.55%. Maximum and minimum TOC content was obtained in MOR-74 and MOR-75 samples respectively which were both deposited in Woodward County. This result supports the idea of Morrow's dynamic depositional conditions. The average TOC values of the Kephart-1 Well core samples is 1.32%. The minimum value of TOC is 0.29% at

8494 ft. and maximum of 2.85% at 8532 ft. in the core. (The TOC content was 3.02% in A-9; however the A-9 data was omitted due to reasons discussed earlier) The TOC values of the two source rock samples from Laverne-State-1 core at Harper County were 19.6% at 7012 ft. and 6.3% 7029 ft., respectively. According to this classification system, the Morrow Shale in the study can be classified as a good source rock in terms of organic richness as average TOC content varies between 1 % and 2% (Figure 19). However, in Harper County, organic richness of the Morrow Shale became excellent. When considering the general TOC trend of the Morrow Shale, the sample in Harper County with a value of 19.6% is considered to be anomalously high, above the expected range for the Morrow. This result does not reflect the geochemical character of the Morrow, and may be due to re-working of organic matter into the original depositional environment.

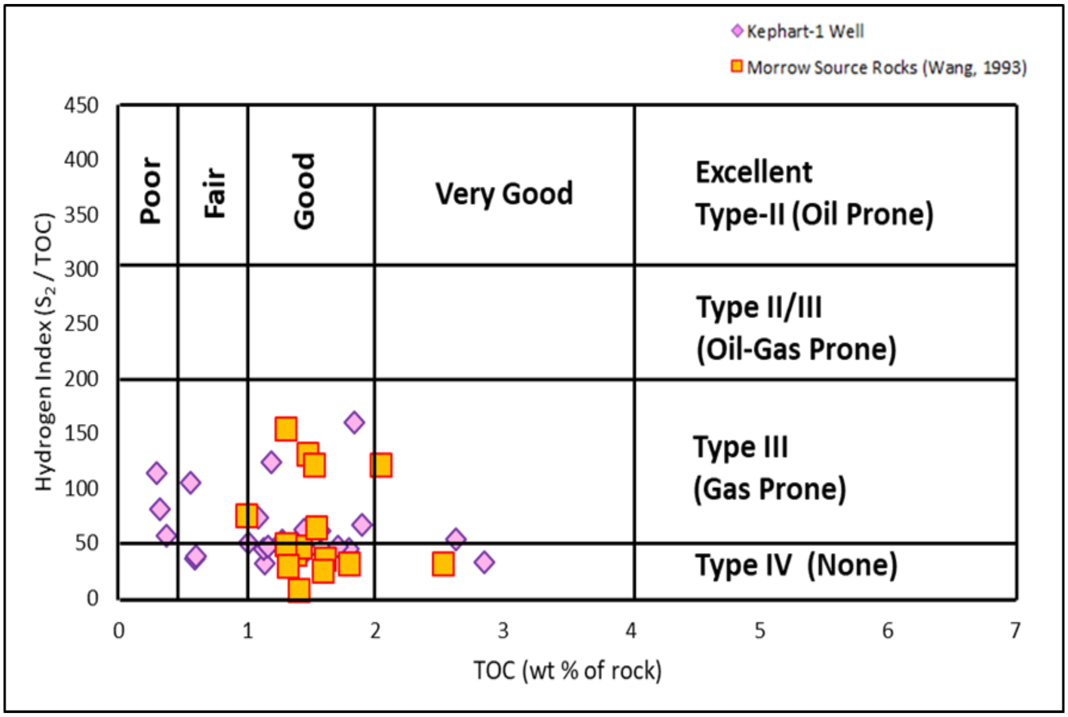


Figure 19. Cross plot of hydrogen index (HI) vs. TOC indicating amount, nature and generation potential of the organic matter.

Because of that reason, H-2 and H-3 samples in this study were not used for organic richness or kerogen type assessments. However, the TOC results of this study support the TOC observation of Joseph Hatch which was published in Higley et al. (2014) study. According to that study, TOC values of the Morrowan Shales from 14 wells in the Anadarko Basin ranged from 0.48 % to 10.71 wt % with an average of 1.72 %. In general, the TOC variance in the Morrow source rocks demonstrates the heterogenic and complex character of the Morrow Formation. Moreover, the TOC log of the Kephart-1 core demonstrates that there is no specific trend in the TOC content of the core samples. The periodic fluctuations in organic matter may be due to frequent sea level changes throughout the depositional history (Figure 20).

4.1.2 Kerogen Classification

Kerogen of the Morrow Shale was characterized by plotting HI and OI values on the Pseudo-van Krevelen diagram as explained in the previous chapter. The HI values of the Morrow source rocks from the Wang (1993) study range from 7 to 155 mgHC/gTOC, with an average of 64 mgHC/gTOC. The HI values of the Kephart-1 core varies between 32 to 160 mgHC/gTOC with an average of 62 mgHC/gTOC. The HI values of the Laverne-State-1 core are 570 for H-2 and 33 for H-3, respectively. As discussed above these anomalous results for the Laverne-State-I Well do not reflect the values commonly reported for the Morrow and have been omitted for the kerogen characterization. When characterizing kerogen, HI values should be evaluated with caution as it might be influenced by thermal maturity. For instance, HI decreases with increasing thermal maturity as the kerogen becomes more depleted in hydrogen during the conversion of organic matter into oil and gas. Therefore, the low range of HI in the Morrow samples can be related to high thermal maturity of the samples.

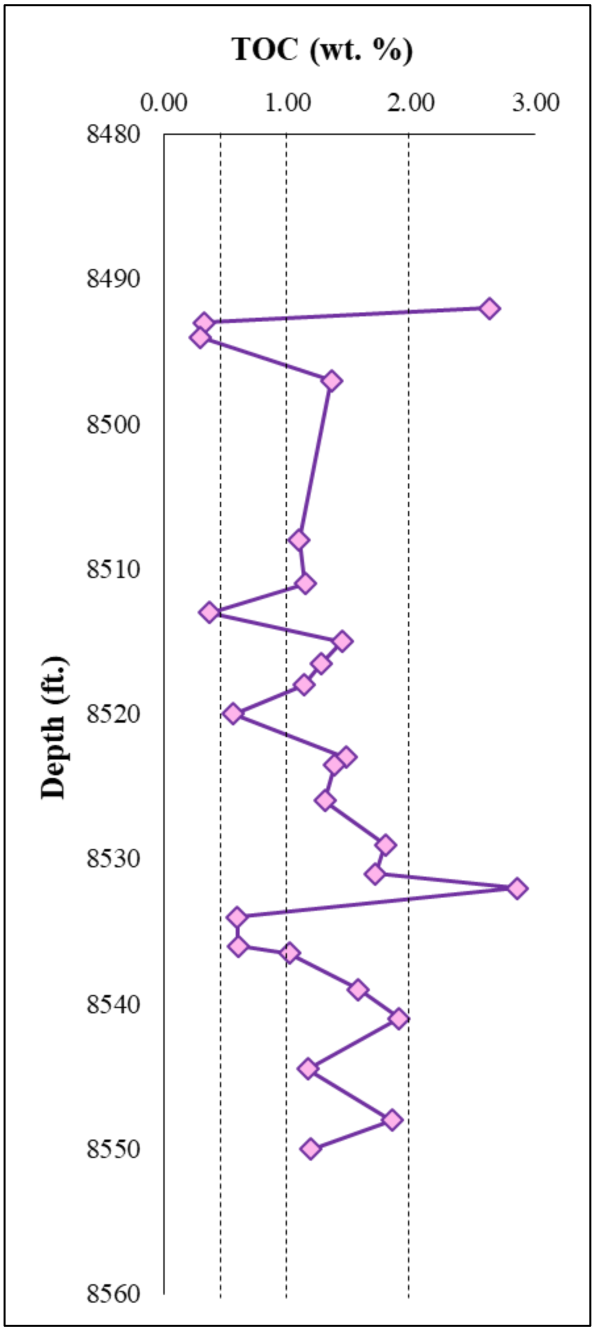


Figure 20. TOC log plot of the Kephart-1 core showing the variance in TOC content with depth.

According to Higley et al. (2014); the HI values of the fourteen Morrow source rock samples range from 15 to 179 mgHC/gTOC with an average value of 46 mgHC/gTOC which is very close to the results of this study. According to the Rock-Eval Pyrolysis data, the Kephart-1 core samples are mainly characterized as Type-III kerogen (only few of them are characterized as Type-IV kerogen) derived from woody terrestrial plants, and potentially generate gas if appropriate conditions prevail (Figure 21).

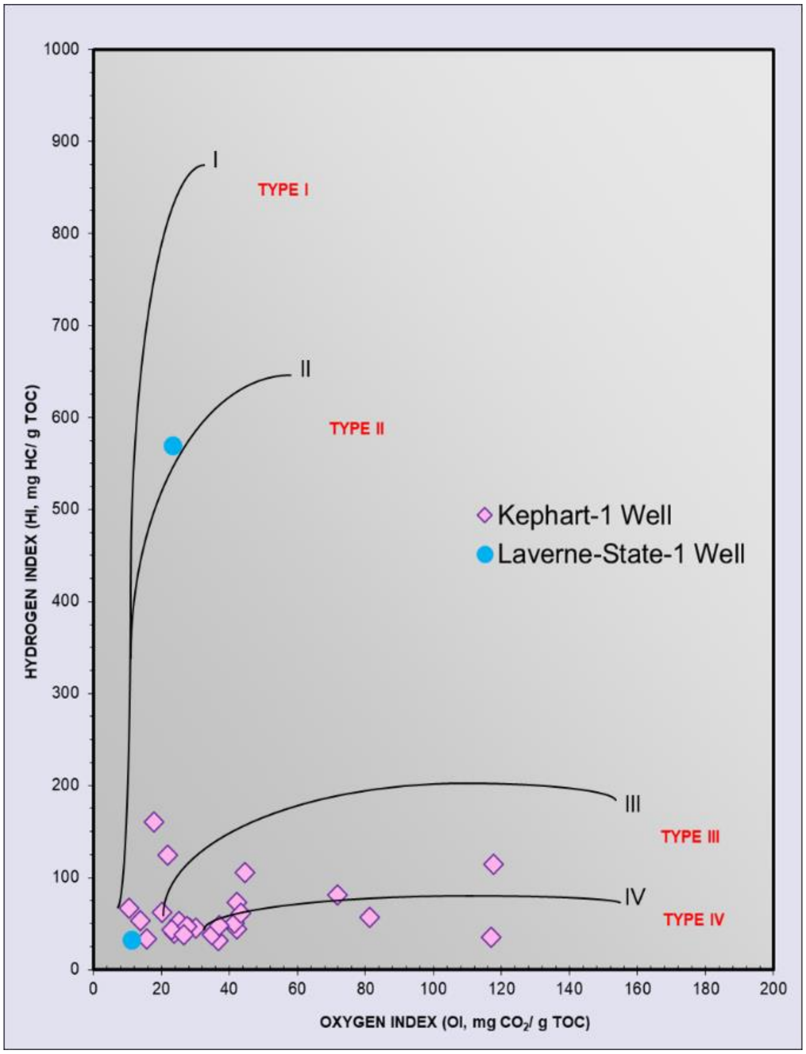


Figure 21. Pseudo-van Krevelen diagram to determine the kerogen type of the Morrow core samples. The Kephart-1 core samples are predominantly Type-III kerogen with mixing of Type-IV kerogen in some of the samples. Laverne-State-1 core sample of H-2 is characterized with Type-II kerogen. Note that Wang (1993) source rock samples could not be plotted due to lack of S_3 data.

Peters (1986) classified source rock generative potential as poor, fair, good and very good based on their TOC and S_2 content. According to his criteria, the S_2 vs. TOC plot in Figure 19 indicates that the Morrow Shale could be characterized as a good source rock. The S_2 vs. TOC plot is also another useful way of determining the kerogen type for immature rocks or early mature rocks (Cornford et al., 1998). The regression line of this plot basically represents HI; thus the results should be evaluated with caution by considering the maturity effect on HI. The plot was used in order to assess the kerogen type of the Morrow source rock samples, which were re-analyzed in this project. According to this plot, most of the Morrow source rock samples are mainly characterized with Type-III kerogen derived from terrigenous plants, whilst a few of them being characterized with inert Type-IV kerogens which have no hydrocarbon generation potential (Figure 22).

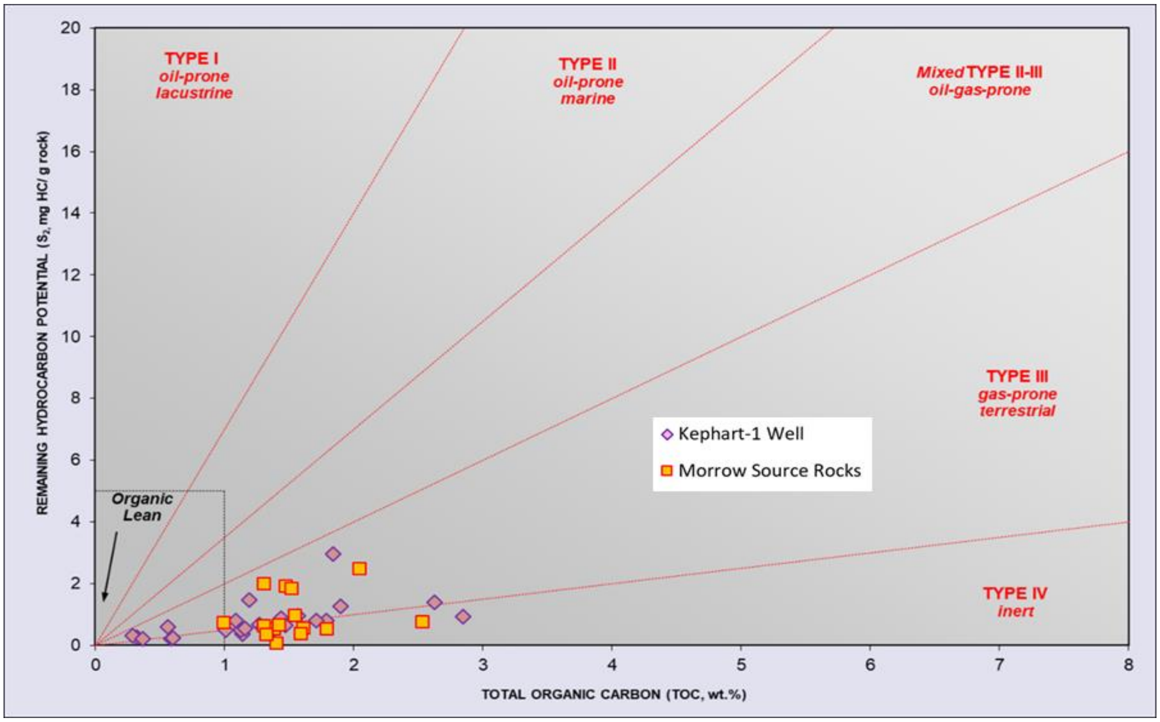


Figure 22. S_2 vs. TOC plot used to determine kerogen type of the Morrow source rock samples in the Anadarko Basin.

4.1.3 Thermal Maturity

Source rock maturation is the degree of alteration of organic matter under the heating process. It can be effected by several factors such as type of organic matter, presence of excess amount of HC present in the rock, mineral composition, mineral content, or burial depth (Atta-Peters, 2014). In this study, thermal maturity of the samples were assessed by using Rock-Eval Pyrolysis results of T_{max}, calculated vitrinite reflectance (%R_c), and production index values and are presented in Table 3 and Table 4. As briefly discussed before, the samples that were not qualified for the screening conditions were rejected from the evaluation (see Table 5 for the conditions).

The T_{max} temperature is one of the parameters used to evaluate the thermal maturity of the rocks. In petroleum exploration, the source rock is considered to be immature if T_{max} is less than 435^{O}C; mature if T_{max} is between 435^{O}C and 470^{O}C; and post-mature if T_{max} exceeds 470^{O}C (Peters and Cassa, 1994). In this study, T_{max} of the source rock samples in the Anadarko Basin ranges from 422^{O}C to 456^{O}C with an average of 439^{O}C indicating that the sources rocks are thermally mature. Peters and Cassa (1994) mentioned that the early oil window corresponds to 435-445^{O}C while the late oil window takes place at 450-470^{O}C. This suggests that the maturity of the organic matter in the Morrow Shale, Anadarko Basin varies between immature to mature (late-oil window) stage. In general, T_{max} values showed a decreasing trend from the southeast to the northwest end of the study area. The reason for this trend is because the burial depth of the Morrow changes significantly due to the asymmetric character of the Anadarko Basin. For instance, while the Morrow was deposited at 15,000 ft. depth in McClain County, it can be found at 7000 ft. depth in Harper County. This, in fact, makes it inappropriate to assign just one maturity trend for the Morrow as it shows significant variation in T_{max} and

%R_c values at different parts of the basin. The average T_{max} value of the Kephart-I core is 454^{O}C and ranges between 436^{O}C to 463^{O}C and the average T_{max} value of the source rocks from Harper County is 436^{O}C (Figure 23). This suggests that based on T_{max} data, the organic matter in the Morrow is thermally mature between the early oil-window and the wet-condensate zone for the core samples analyzed.

Calculated vitrinite reflectance, %R_c, is another useful parameter to assess the maturity of the source rocks. Jarvie et al. (2001) proposed a conversion formula to calculate vitrinite reflectance (%R_c) from T_{max} data. Although the equation was originally proposed for the Barnett Shale, it is now accepted as a valuable maturity indicator worldwide. The conversion formula is as follows:

$$R_c\,\%\ \text{(calculated vitrinite reflectance)} = [(0.018)*T_{max}] - 7.16$$

(Jarvie et al., 2001)

Andrews (1999) proposed that the degree of maturation of the Morrow Formation varies significantly with depth in Oklahoma. He mentioned that while % R_0 of the samples from the deeper Anadarko Basin exceed 2.5 %R_0, this number drops to 0.5 through the Oklahoma Panhandle where the Morrow thins significantly compared to the deeper Anadarko Basin. Thus, the Morrow can be immature to overcooked dependent on burial depth. In this study, calculated vitrinite reflectance values also support Andrews (1999) results. For example, average %R_c of the 15 source rock samples from the Anadarko Basin is 0.73, ranging between 0.44 %R_c at 7943 ft. and 1.05%R_c at 10816 ft. According to these results, the thermal maturity of the Morrow in the Anadarko Basin varies between immature to the late-oil window. The results showed that the maturity of the Morrow is

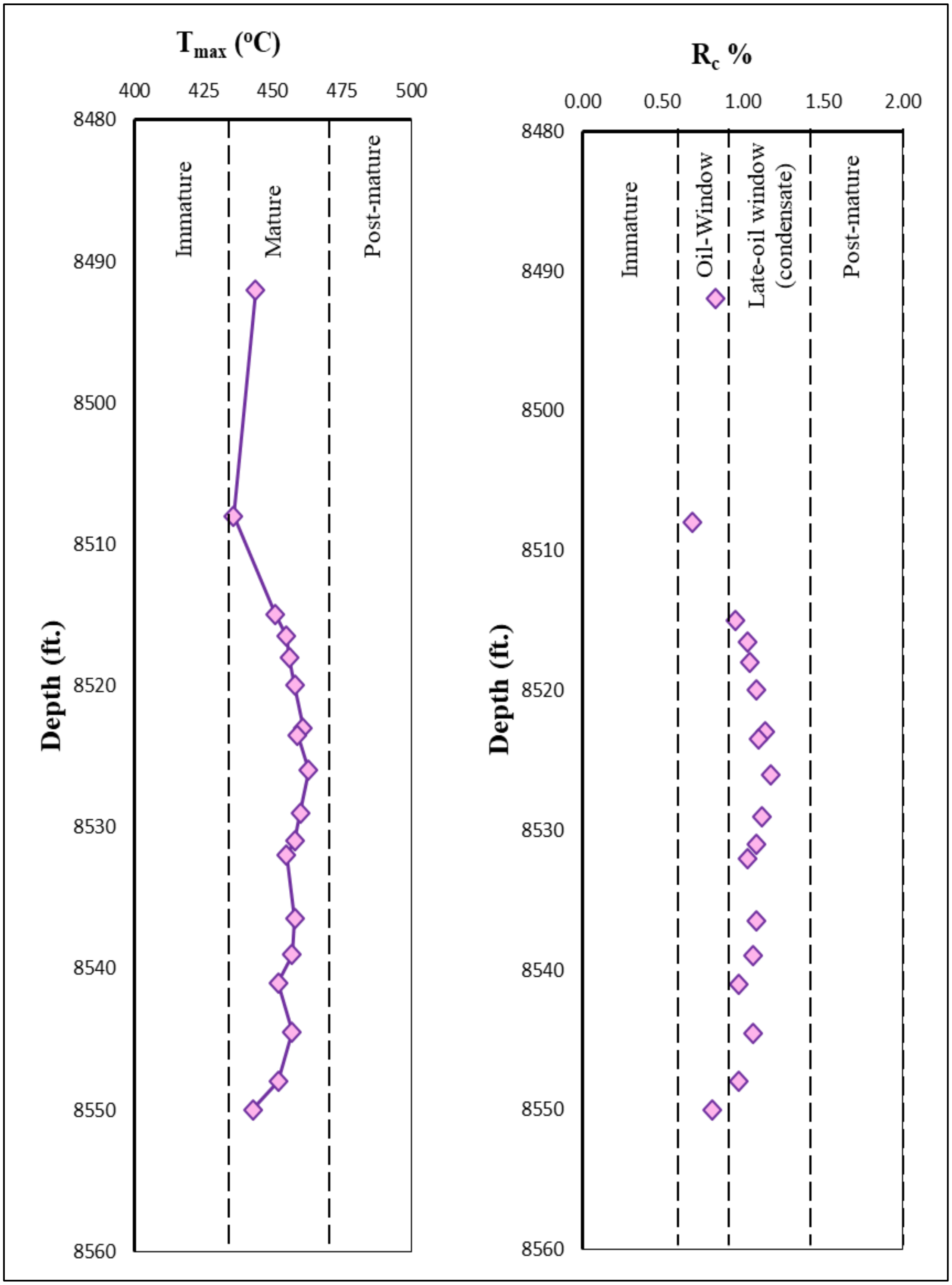


Figure 23. T_{max} and calculated R_c % logs of the Kephart-I core showing the maturity trend in the core.

highly dependent on the burial depth as a decreasing maturity trend from the deeper Anadarko Basin through the Oklahoma Panhandle area is observed in the samples. The Kephart-I core from Blaine County is in the late oil window with an average % R_c value of 1.02 that varies between 0.69-1.17 % Rc through the core (Figure 23). The source rock samples from Harper County, which is at the northwestern end of the study area, are in the peak oil window with average 0.68 % R_c.

The last thermal maturity parameter used in this study was the production index (PI). In source rocks, the production index is expected to increase with increasing thermal maturity in the absence of expulsion (Espitalié et al., 1977). However, change in the organic facies, non-indigenous oil migration into sediment or oil expulsion can cause some anomalies in the PI values. According to Peters (1986), organic matter is considered to be immature if the PI value is less than 0.2; mature (in the oil-window) if it is between 0.3-0.4 and contaminated by another hydrocarbon if it is more than 0.5. In this study, combining production index data with T_{max} provided valuable information about the hydrocarbon generation zone and potential contamination of the source rock (Figure 24). According to the cross plot, the Morrow source rock samples demonstrate a transitional trend between immature to late oil-window based on increasing burial depth. The Kephart-1 core samples, however, mainly plotted in the late-oil window. The A-10 sample, may have a potential contamination problem although it was not rejected based on the RE screening parameters (Table 5). Finally, the H-2 sample from Harper County is not thermally mature for HC generation, while the H-3 sample plots in the HC generation zone.

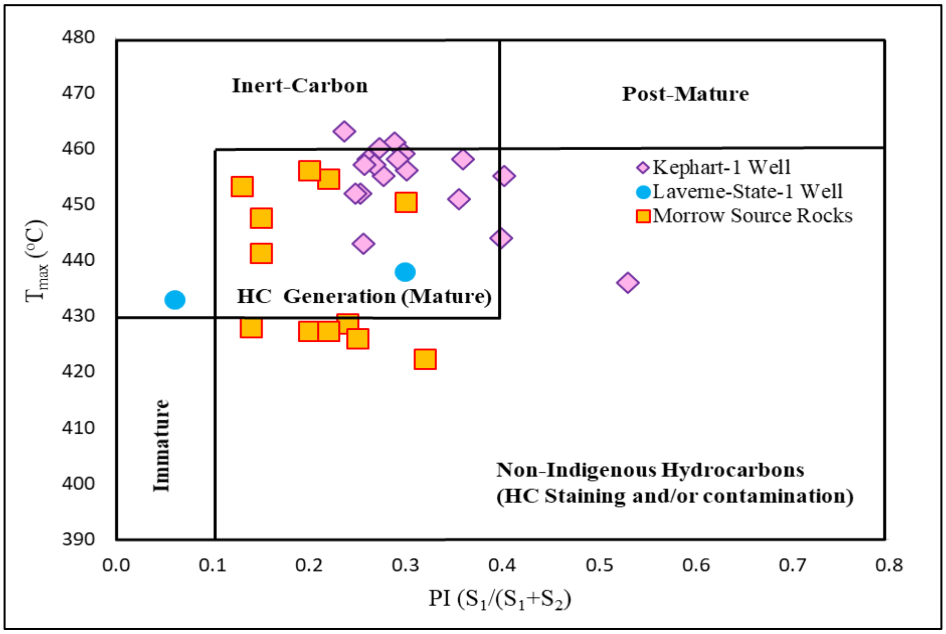


Figure 24. T_{max} vs. PI plot showing hydrocarbon generation zones of organic matter in the Morrow Shales.

4.2 Fraction Yields

The source rock samples were fractionated into aliphatic, aromatic and polar compounds. Fraction yield percentages of the studied samples are presented in Table 2. The relative abundance of the aliphatic, aromatic and polar fractions of the samples were used to construct a ternary diagram (Figure 25). In Kephart-I Well, the aliphatic fraction ranges between 38%-83% while the aromatic compounds range between 7%-45% in the Kephart-I rock extracts. In Harper County, H-2 rock extract, which has an abnormally high TOC content, the aromatic fraction is relatively abundant while the H-3 extract is dominated by aliphatic compounds. The percentages differ significantly from the Wang (1993) fraction yields. For example, the average total aliphatic and aromatic fractions in the Wang (1993) study were approximately 58% and the NSO compounds were the dominant fraction in most of the rock extracts in the Wang (1993) study (Table 2). The possible reason for this contrast might be related to the fractionation methods being different. For example, Wang (1993) used the thin layer chromatography (TLC) method for the fractionation of the samples which is an older fractionation method compared to column chromatography and provides less reliable data for quantitative purposes (Cserháti and Forgács, 1997). Cserháti and Forgács (1997) mentioned that TLC has been originally developed as a qualitative method and its original form is only suitable for the semi-quantitative analysis and added that there is also possible volatility losses in TLC due to air exposure of samples (Cserháti and Forgács, 1997). Alternatively, the other possible reason for the difference in the fractionation yields might be related to sample preparation. For example, high evaporation rates might cause elimination of the *n*-alkanes and result in the difference between data sets.

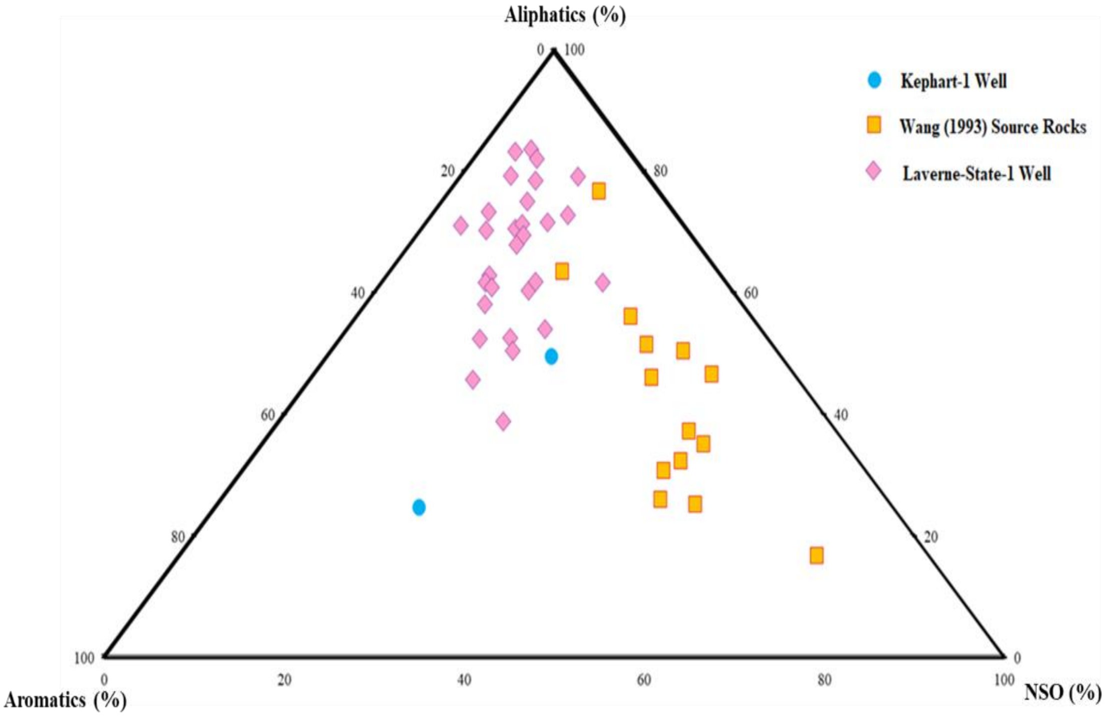


Figure 25. Ternary Diagram of the fraction yield data for the Morrow source rock samples

4.3 Biomarker Analysis

Biomarkers are organic compounds in sediments, sedimentary rocks and oils whose carbon skeletons are related to functionalized compounds of formerly living organisms (Waples and Machihara, 1991). Biomarker fingerprinting can provide valuable information about type of organic matter, depositional conditions, age-dating, thermal maturity, migration history and degree of biodegradation (Wang et al., 2004). Their occurrence, distribution and abundance can be monitored by GC, GC-MS and GC-MS-MS analysis.

4.3.1 n-Alkanes and Isoprenoids

Certain n-alkanes and isoprenoid ratios from source rocks and oils can be used to interpret thermal maturity, degree of biodegradation, source input and redox conditions of the depositional environment (Peters et al., 2005). Nonetheless, it should be noted that these interpretations can be easily effected by various factors. For instance, redox conditions and type of organic matter input affect the isoprenoid distribution while they can be misinterpreted if the thermal maturation and biodegradation level of the samples are not considered (Bray and Evans, 1961). *n*-Alkanes range from C_1 and extend beyond C_{120} and can be easily detected by GC. Koons et al. (1965) reported the lowest molecular weight n-alkane in plants as *n*-heptane (C_7H_{16}) and the highest as dohexacontane ($C_{62}H_{126}$; Tissot and Welte, 1984). *n*-Alkane fingerprinting provides valuable information about the origin of organic matter. For instance, odd over even carbon number predominance of the medium to high molecular weight n-alkanes ($>C_{25}$) generally indicates higher plant input (Tissot and Welte, 1984) while high concentration of low molecular weight alkanes ($<C_{22}$) compared to high molecular weight n-alkanes ($>C_{25}$) may be indicative of marine source input (Jacobson et al., 1988; Wang and Philp, 1997).

Moreover, even over odd predominance of n-alkanes is often an indication for carbonate source rocks whose organic matter is mainly derived from highly reducing environments (Moldowan et al., 1985; Wang and Philp, 1997). Bray and Evans (1961) proposed that odd over even predominance of the carbon atoms can be assessed by the "Carbon Preference Index" (CPI) which is the ratio of odd carbon number n-alkanes over even carbon number n-alkanes. Scalan and Smith (1970) defined another parameter, "Odd-Even Predominance" (OEP), to measure the odd over even predominance of the carbon atoms with increasing molecular weight (Tissot and Welte, 1984). Both CPI and OEP can be used to estimate thermal maturity as they both decrease with the increasing maturity (Wang and Philp, 1997). CPI and OEP ratios used in this study are given in the following equations and were calculated by using the peak areas of the n-alkanes in gas chromatograms.

$$CPI = \left[\frac{C_{23} + C_{25} + C_{27}}{C_{24} + C_{26} + C_{28}} + \frac{C_{25} + C_{27} + C_{29}}{C_{24} + C_{26} + C_{28}}\right] \times \frac{1}{2} \qquad \text{Marzi et al. (1993)}$$

$$OEP = \frac{C_{21} + 6C_{23} + C_{25}}{4C_{22} + 4C_{24}} \qquad \text{Peters et al. (2005)}$$

The CPI for most of the Morrow source rock samples of the Wang (1993) study are very close to 1.0 with an average of 1.04. However, MOR-33 from Roger Mills and MOR-57 from Dewey County have CPI values less than 1.0 which may indicate the increasing carbonate content in the depositional area. Moreover, CPI of the samples from Kephart-I and Laverne-State-I cores are all greater than 1.0 with average value of 1.09 for both data sets.

The average OEP value of the Wang (1993) source rock samples was 0.99 and most of the samples are approximately 1.0, although a few Morrow Shale samples have OEP values less than 1.0. This may be due to the influence of carbonate beds intercalated with the shale beds. Alternatively, the OEP value of the Kephart-I ranges from 0.88-1.12 with an average of 1.02 and OEP of the Laverne-State-I well samples of H-2 and H-3 are 1.04 and 0.98, respectively.

Another effective proxy for interpreting the type of source material is the terrigenous/aquatic ratio (TAR) which was first formulated by Bourbonniere and Meyers (1996) as the following equation. This ratio indicates the relative proportion of the terrigenous vs. aquatic organic matter input into the depositional environment but it is susceptible to secondary processes such as biodegradation or thermal maturity (Peters et al., 2005).

$$TAR = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}$$

Bourbonniere and Meyers (1996)

The TAR values of the Wang (1993) Morrow source rocks ranges between 0.03-1.63 with an average of 0.30. The average TAR values of the Kephart-I and Laverne-State-I well are 0.08 and 0.2, respectively. TAR shows slight changes through the Kephart-I core with the exception of 8513 ft. at which terrigenous influx of the core significantly increases (Figure 26). Terrestrial higher plants in the depositional environment contribute to odd numbered high molecular weight n-alkanes ($>C_{25}$) and therefore result in higher TAR values.

In general, the results being significantly different at each location supports the dynamic depositional conditions of the Morrow and periodic terrigenous influx to the depositional environment during deposition.

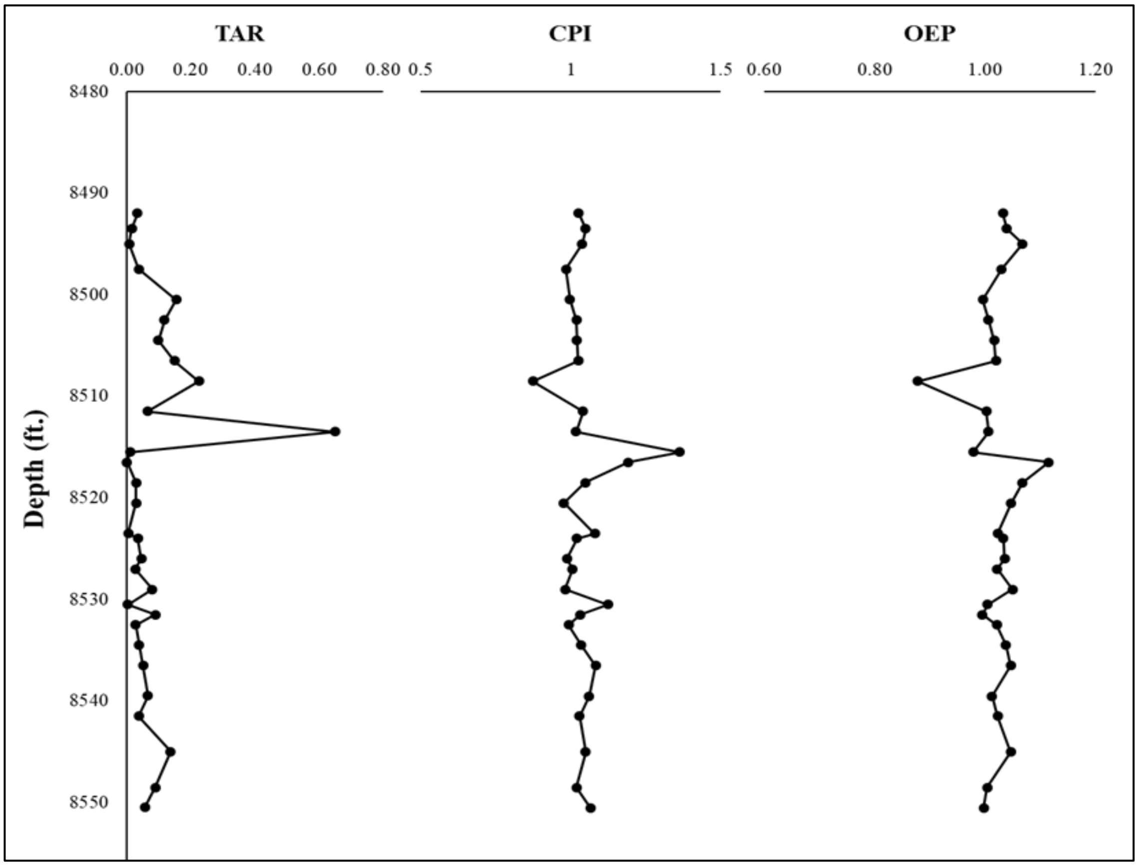


Figure 26. TAR, CPI and OEP values vs. depth for the Kephart-1 Rock Extracts

The Morrow is typically characterized by a bimodal n-alkane distribution, yet unimodal and trimodal distributions are also observed in highly mature and/or biodegraded samples (MOR 74, MOR 33; Figure 27). The presence of higher molecular weight n-alkanes (> C_{21}) in the samples indicates a terrestrial higher plant input during

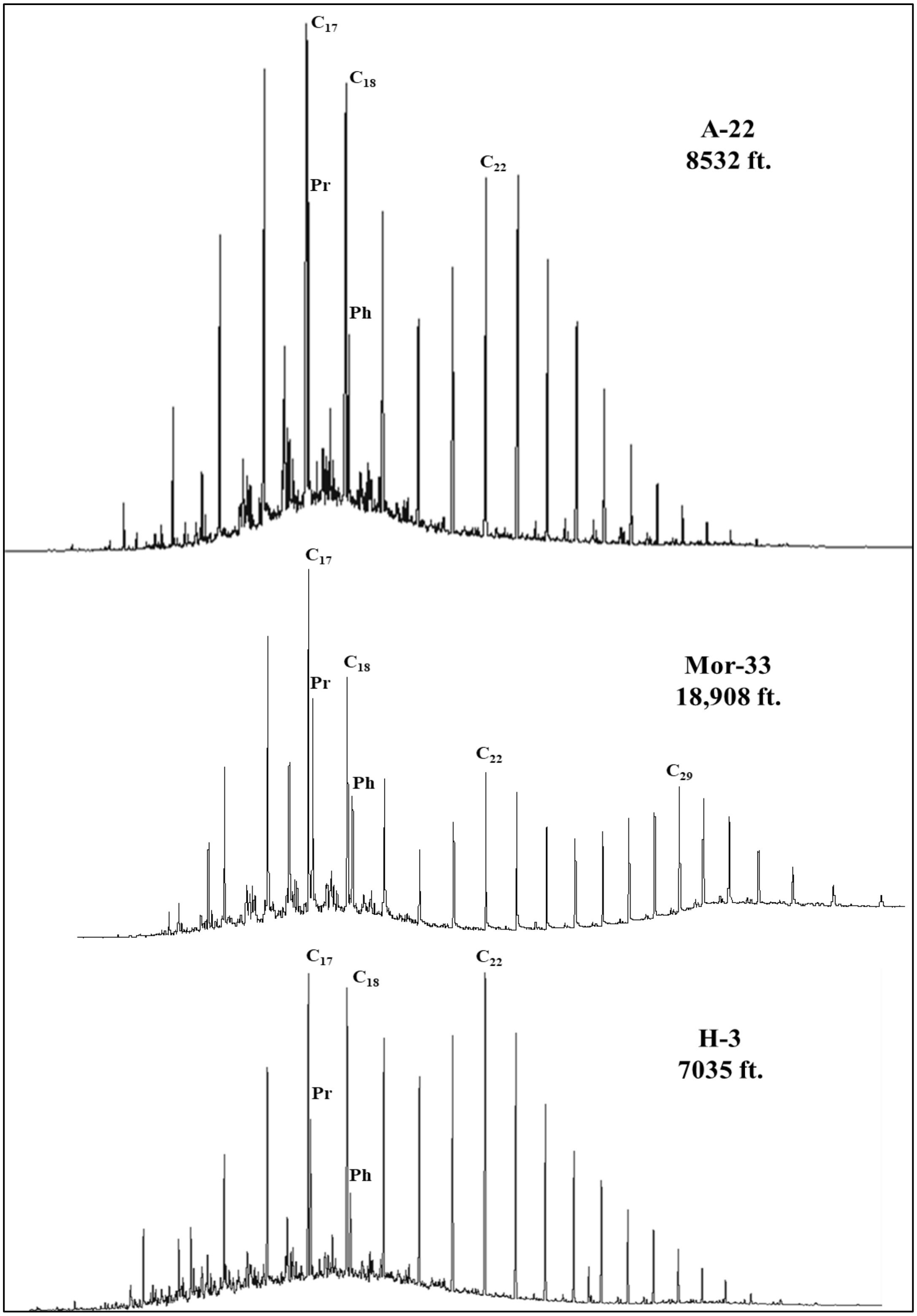


Figure 27. Gas Chromatograms showing the *n*-alkane distributions of the Morrow Shale samples (Pr: pristane, Ph: Phytane)

the deposition of the Morrow which supports the fact that the Morrow was deposited at a near-shore transitional (mixed type) depositional environment and periodically subjected to terrigenous influx. Moreover, the samples with a narrow unimodal n-alkane distribution and C_{17} (**I**: see structures in Appendix A) and/or C_{18} (**II**) predominance and lack of higher molecular weight n-alkanes may indicate low terrigenous input into the depositional environment at that location, or elevated maturity of the sample. Most of the Morrow samples maximize at C_{22} which might be due to the specific environmental conditions prevailed during the deposition of the Morrow was favorable for the occurrence of a specific algae type (Schenck and Havenaar, 1969).

The most commonly used isoprenoids pristane (Pr; **III**) and phytane (Ph; **IV**) provide valuable information about the redox conditions during deposition of the source rock. It is widely accepted that they are derived from the sidechain of chlorophyll bearing organisms although different precursors have been also proposed such as archaebacterial ether lipids for both of the isoprenoids or tocopherols for pristane (Didyk et al., 1978; Brassell and Eglinton, 1983; Goossens et al., 1984; Koopmans et al., 1999). The oxidation-reduction conditions of the depositional environment may be indicated by differences in the ratio of Pr/Ph. For example, low Eh (oxidizing) conditions are favorable for the occurrence of pristane, while high Eh (reducing) depositional environment favors the occurrence of phytane (Powell and McKirdy, 1973). Didyk et al. (1978) proposed that the Pr/Ph ratio can provide valuable information about organic matter type and depositional environment conditions as isoprenoids are less susceptible to thermal cracking or biodegradation. Furthermore, Pr and Ph can be also used to interpret maturity and extent of biodegradation when combined with n-alkanes C_{17} and C_{18}, respectively

(Shanmugam, 1985; Waples, 1985). As generally accepted, Pr/Ph<1 is indicative of anoxic depositional conditions when supported with other geochemical data such as high porphyrin and sulfur content (Peters et al., 2005). Pr/Ph values between 1 and 3 indicates a sub-oxic environment which was periodically influenced by different redox conditions and Pr/Ph >3 is indicative of oxic depositional conditions with terrigenous organic matter influx.

The Pr/Ph ratios of most of the Morrow source rock samples from the Wang (1993) study are greater than 1.0 (Table 6). The only exception is MOR-74 sample whose Pr/Ph ratio is slightly less than 1.0. The results being greater than one indicate that the Morrow was deposited in a transitional depositional environment during which oxic and anoxic conditions alternatively prevailed. Thus, the depositional environment was supplied by both terrestrial and marine organic input. The Pr/Ph ratio of the Kephart-I well is greater than 1 throughout the core with the exception of the 8516-8495 ft. interval (Figure 28; Table 6). The Pr/Ph ratios of this interval are less than 1.0 indicating that anoxic conditions prevailed during deposition of this interval. The Pr/Ph ratios of the two core samples (H-2 and H-3) from Laverne-State-I well are 4.35 and 1.42, respectively, indicating that oxic to suboxic depositional conditions with terrigenous organic matter input prevailed during deposition of the Morrow in Harper County. Figure 29 shows the cross plot of Pr/n-C_{17} vs. Ph/n-C_{18} in which samples plotted in a transitional depositional setting with mixed organic matter. The plot also shows that the samples were not biodegraded since if they were, Pr/n-C_{17} vs. Ph/n-C_{18} ratio would be expected to be elevated since n-alkanes are removed before the isoprenoids in biodegraded organic matter.

Table 6. Calculated isoprenoid, tricyclic and pentacyclic terpane values for the Morrow source rock samples

Samples	Pr/*n* C_{17}	Ph/*n* C_{18}	Pr/Ph	C_{20}/C_{23}	C_{19}/C_{23}	C_{23}/C_{30}	C_{26}/C_{25}	Ts/ (Ts+Tm)	C_{31}-22S/ (22R+22S)
A-1	0.40	0.32	1.44	1.30	1.07	0.27	0.76	0.32	0.61
A-2	0.57	0.44	1.14	0.93	0.61	4.28	0.69	0.52	0.61
A-3	0.69	0.55	0.82	1.53	0.99	3.00	0.70	0.45	0.58
A-4	0.70	0.61	0.85	0.72	0.42	2.30	0.79	0.47	0.55
A-5	0.60	0.49	0.71	0.39	0.18	0.69	1.01	0.38	0.57
A-6	0.60	0.51	0.63	0.47	0.21	0.73	0.99	0.40	0.57
A-7	0.62	0.47	0.70	0.42	0.17	0.50	0.21	0.41	0.56
A-8	0.65	0.55	0.56	0.40	0.20	0.57	1.09	0.41	0.55
A-9	0.55	0.49	0.73	0.35	0.15	0.37	1.16	0.39	0.60
A-10	0.61	0.51	0.82	0.64	0.42	1.95	0.85	0.48	0.57
A-11	0.61	0.55	0.80	0.31	0.16	0.63	1.04	0.42	0.58
A-12	0.83	0.58	0.71	0.90	0.74	1.91	0.67	0.37	0.60
A-13	0.73	0.51	0.75	1.00	0.71	1.87	0.70	0.40	0.55
A-14	0.58	0.43	1.05	1.04	0.89	0.84	0.73	0.38	0.59
A-15	0.57	0.46	1.08	1.63	1.58	0.87	0.80	0.38	0.56
A-16	0.54	0.45	1.47	1.16	1.02	0.92	0.99	0.39	0.59
A-17	0.48	0.50	1.11	2.02	2.21	0.59	0.73	0.32	0.59
A-18	0.48	0.41	1.41	1.67	1.95	0.49	0.76	0.28	0.59
A-19	0.52	0.44	1.31	1.36	1.30	0.60	0.82	0.38	0.57
A-20	0.47	0.39	1.54	1.20	1.14	0.70	0.74	0.34	0.59
A-21	0.50	0.43	1.52	0.90	0.77	0.98	0.79	0.32	0.60
A-22	0.50	0.38	1.53	0.97	0.94	0.50	0.81	0.29	0.58
A-23	0.53	0.39	1.51	1.21	1.16	0.32	1.09	0.27	0.59
A-24	0.82	0.56	1.13	0.95	0.74	1.39	0.76	0.44	0.60
A-25	0.48	0.40	1.26	1.03	1.17	0.97	0.67	0.38	0.60
A-26	0.49	0.40	1.54	0.86	0.78	0.42	0.78	0.36	0.58
A-27	0.44	0.39	1.57	1.07	1.02	0.32	0.78	0.30	0.58
A-28	0.48	0.38	1.81	0.48	0.40	0.51	0.82	0.39	0.59
A-29	0.57	0.55	1.34	0.64	0.55	0.62	1.12	0.56	0.34
A-30	0.60	0.52	1.54	0.64	0.51	0.53	0.91	0.87	0.59
H-2	2.47	0.60	4.35	4.50	2.61	0.02	2.63	0.10	0.60
H-3	0.53	0.45	1.42	1.27	1.74	0.10	1.68	0.11	0.59
MOR 33	0.74	0.60	1.58	0.59	0.43	1.10	0.68	0.49	0.58
MOR 39	0.57	0.51	1.83	1.12	0.98	1.27	0.41	0.47	0.53
MOR 41	0.51	0.45	1.76	0.97	1.11	1.08	0.59	0.44	0.42
MOR 75	0.63	0.54	1.83	1.68	1.28	0.13	2.57	0.06	0.58
MOR 2	0.62	0.45	1.41	0.89	0.53	1.18	0.35	0.69	0.50
MOR 11	0.59	0.58	1.49	0.82	0.78	0.29	0.47	0.37	0.54
MOR 57	0.48	0.34	1.65	0.90	0.93	0.16	2.19	0.49	0.53
MOR 74	0.59	0.55	0.97	0.33	0.32	0.74	1.05	0.46	0.51
MOR 91	0.47	0.51	1.19	0.73	0.65	0.72	1.78	0.61	0.46
MOR 68	0.54	0.38	1.75	0.21	0.09	1.06	0.32	0.61	0.55
MOR 16	0.82	0.55	1.38	0.51	0.23	0.26	0.32	0.41	0.49
MOR 64	0.71	0.57	1.31	0.51	0.41	0.53	0.33	0.74	0.59
MOR 66	0.81	0.62	1.48	0.23	0.17	0.28	0.51	0.78	0.56
MOR 43	0.59	0.56	1.25	0.46	0.37	0.14	0.98	0.50	0.57
MOR 86	0.50	0.40	1.32	0.28	0.15	1.13	0.35	0.31	0.57

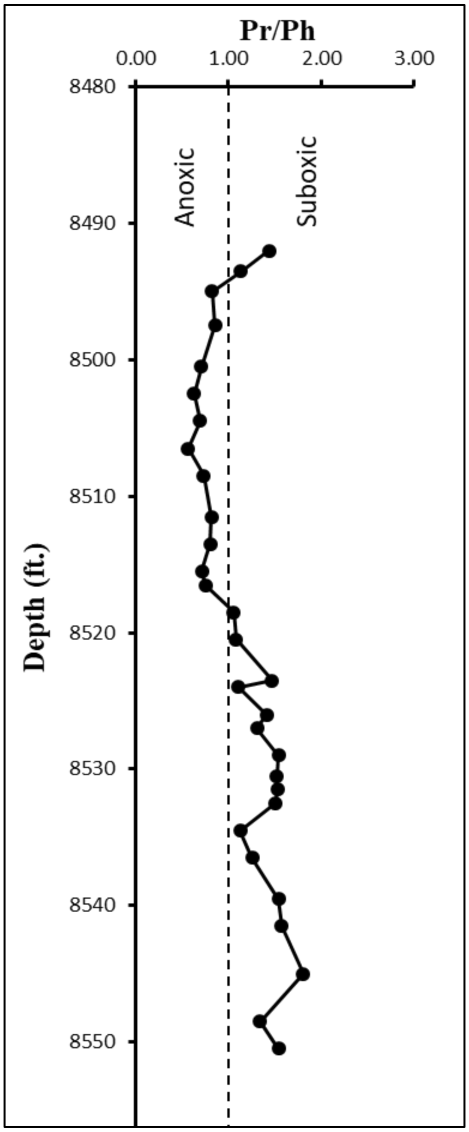


Figure 28. Pr/Ph ratio plotted against depth for the Kephart-I Well.

4.3.2 Bicyclic Sesquiterpanes

The occurrence of bicyclic sesquiterpanes in crude oils and sediments have been reported by several authors (Philp et al., 1981; Alexander et al., 1983; Weston et al., 1989; Yang et al., 2008). Alexander et al. (1984) proposed that widespread occurrence of drimanes, such as 8β (H) drimane (**V**) and 8β (H) homodrimane (**VI**), is related to the fact that they are derived from a ubiquitous source. Weston et al. (1989) stated that drimanes are bacterial degradation products of hopanoids during diagenesis while the sesquiterpane

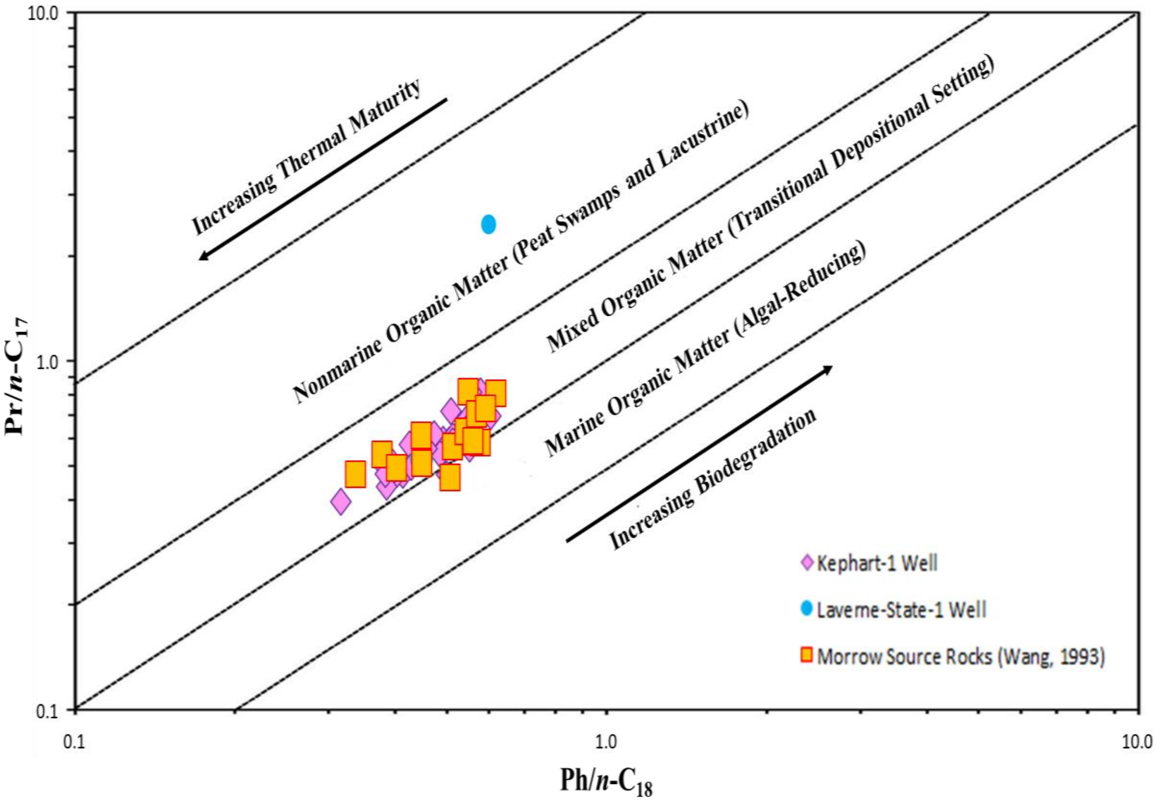


Figure 29. Cross plot of Pr/*n*-C_{17} vs. Ph/*n*-C_{18} shows the Morrow samples falling into mixed organic matter zone (*n*-C_{17}: C_{17} normal alkane; *n*-C_{18}:C_{18} normal alkane)

4β-eudesmane (**VII**) is derived from land plants (Alexander et al., 1984; Weston et al., 1989). The identification of C_{15} and C_{16} sesquiterpanes in the Morrow samples, apart from the 4β-eudesmane, indicates the bacterial contribution to the organic matter during deposition of the Morrow. Moreover, the occurrence of 4β-eudesmane in most of the studied samples supports the contribution of land plant material into the depositional environment. The C_{15}-C_{16} sesquiterpanes distribution were identified by the partial fragmentogram of the m/z 123 ion (Figure 30; Table 7).

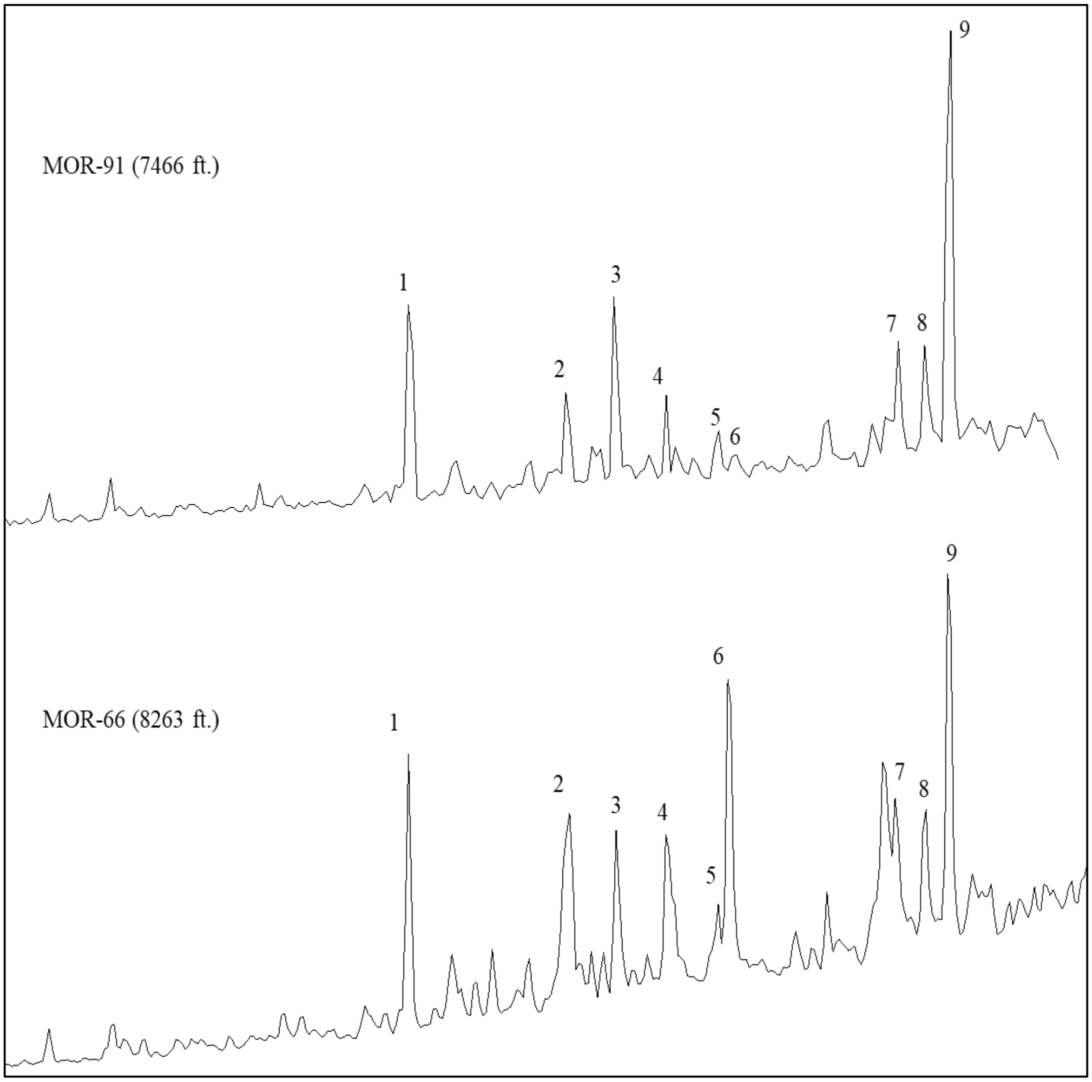


Figure 30. Partial fragmentogram of the m/z 123 ion showing the sesquiterpane distribution. Identification of the compounds given in the Table 7.

Table 7. (m/z 123) Sesquiterpane Identification

Peak Number	Compound
1	C_{15} Sesquiterpane
2	C_{15} 4β(H)-Eudesmane
3	C_{15} Sesquiterpane
4	C_{15} 8β(H)-Drimane
5	C_{15} Sesquiterpane
6	C_{15} 8α(H)-Drimane
7	C_{16} Sesquiterpane
8	C_{16} Sesquiterpane
9	C_{16} 8β(H)-Homodrimane

4.3.3 The Tricyclic Terpanes

Terpanes are one of the most common biomarker group found in the saturate fractions of source rocks and oils. They are not only useful for correlation purposes but also for maturity, depositional environment, organic input and migration assessment (Didyk et al., 1978; Wang et al., 2012; Zhang and Philp, 2012; Tao et al., 2015). Each terpane family exists as a homologous series with numerous isomers and epimers and each of them have different utilities in geochemistry. However, only the tricyclic and the pentacyclic terpane families will be discussed under the scope of this project.

The tricyclic terpane series starts with C_{19} and has been known to extend at least up to C_{54} as proposed by De Grande et al. (1993). However, they are commonly identified up to C_{29} as an extended series and are often concealed by pentacyclic hopanes in m/z 191 ion chromatograms (Tao et al., 2015). Despite their widespread occurrence, the origin of the tricyclic terpanes has been debated for a long time. For instance, Ourisson et al. (1982) and Heissler and Ladenburger (1988) suggested that the precursors of the tricyclic terpanes (for $< C_{30}$) are C_{30} isoprenoids which may be derived from lipids in prokaryotic membranes. Alternatively, they were proposed to be the main constituents of *Tasmanites*, a kind of primitive algae, by Aquino Neto et al. (1989); Volkman et al. (1989) and Azevedo et al. (1992). The tricyclic terpanes are thermally more stable than the hopanes and therefore the ratio of tricyclic terpanes to hopanes was suggested to use as maturity indicator (Peters and Moldowan, 1993). The ratio increases with the increasing maturity in the extent of late oil window (Farrimond et al., 1999). Certain tricyclic terpane ratios can provide valuable information on depositional environment, organic matter input and water salinity. To begin with, C_{19} and C_{20} tricyclic terpanes are suggested to be derived from diterpenoids produced from vascular plants (Barnes and Barnes, 1983; Noble et al.,

1986) while C_{23} is commonly associated with oils with marine organic input (Tao et al., 2015). Thus, C_{19}/C_{23} and C_{20}/C_{23} ratios are useful to assess the terrigenous vs. marine organic matter contribution to the depositional environment (Hanson et al., 2000) while the C_{23} tricyclic terpane to C_{30} hopane ratio can be useful to indicate marine algal input to the depositional environment (Chester, 1990). Moreover, C_{22}/C_{21} and C_{24}/C_{23} terpane ratios can be facies dependent (Clark and Philp, 1989; Liu et al., 2017). The higher values (>0.6) can be interpreted as a carbonate tendency for the source of oil or extracts (Clark and Philp, 1989) while smaller values (<0.6) can be interpreted as clastic tendency for the source rocks or oils. Finally, the C_{26}/C_{25} ratio can be useful to distinguish marine vs. lacustrine oils (Peters et al., 2005) For example, a C_{26}/C_{25} ratio greater than 1.0 may indicate possible lacustrine source rocks and/or hypersalinity while smaller values can be interpreted as possible marine source rocks with moderate or low paleosalinity of the depositional environment (Schiefelbein et al., 1999; Volk et al., 2005).

The Morrow source rock extracts from Wang (1993) are characterized by higher pentacyclic terpane concentrations (hopanes) compared to tricyclic terpanes while some of the highly mature samples are dominated by tricyclic terpanes. The tricyclic terpanes of the Wang (1993) samples typically range from C_{19} to at least C_{29} while C_{23} is the most abundant tricyclic terpane among them. The C_{19}/C_{23} and the C_{20}/C_{23} ratios of the samples are highly variable within the Anadarko Basin with the average values of 0.56 and 0.68; respectively (Table 6). For example, C_{19}/C_{23} and C_{20}/C_{23} values of the MOR-39 sample from Canadian County, MOR-41 from Blaine County and MOR-75 sample from Woodward County are close to greater than 1.0. Moreover, C_{23} (tricyclic terpane)/C_{30} (hopane) values for these samples are 1.27, 1.08 and 0.13, respectively. The results show that MOR-39 and MOR-41 samples probably belonged to a transitional depositional environment with a mixed type of terrestrial and marine organic matter input while MOR-75 was probably deposited in a terrestrial environment. Alternatively, C_{19}/C_{23} and C_{20}/C_{23} values of the MOR-33 sample from Roger Mills County, MOR-86 sample from Woodward County and the MOR-68 sample from Dewey County are smaller than 0.25 with C_{23}/C_{30} values greater than 1.0 strongly indicating that the marine depositional environment prevailed during deposition of these samples. In general, the results indicate that the organic matter type and depositional environment conditions alternated frequently during the deposition of the Morrow as was geologically interpreted above. The C_{26} tricyclic terpane was more abundant than C_{25} tricyclic terpanes in the MOR-57, MOR-75 and MOR-91 samples which was proposed to be diagnostic characteristic of the lacustrine facies by Schiefelbein et al. (1999). According to the depositional environment classification based on the C_{26}/C_{25} ratio (Tao et al., 2015), MOR-57 and MOR-75 could have been deposited in a lacustrine environment while MOR-91 was possibly deposited in a transitional/lagoonal depositional environment. Furthermore, these conclusions are supported by the higher concentrations of the C_{24} tetracyclic terpane, typically associated with a carbonate or evaporitic depositional environment (Clark and Philp, 1989; Gong et. al., 2007). Thus, relatively higher C_{24} tetracyclic terpane concentration in the MOR-91 samples compared to other samples suggests that this sample was probably deposited in shallow lagoon dominated by evaporitic carbonates. Based on the lower C_{26}/C_{25} ratios and the C_{24} tetracyclic terpane concentrations in the remaining source rock samples, a marine depositional environment with low to moderate salinity conditions prevailed in most of the sample locations in the Anadarko Basin.

In the Kephart-I core, the average C_{19}/C_{23} and C_{20}/C_{23} and C_{23}/C_{30} values are 0.81, 0.94, and 1.02, respectively. The fluctuations in the ratios through the core demonstrate the changes in the type of organic matter input over time (Figure 31; Table 6). The results indicate that the Kephart-I well was deposited at the transitional/nearshore environment

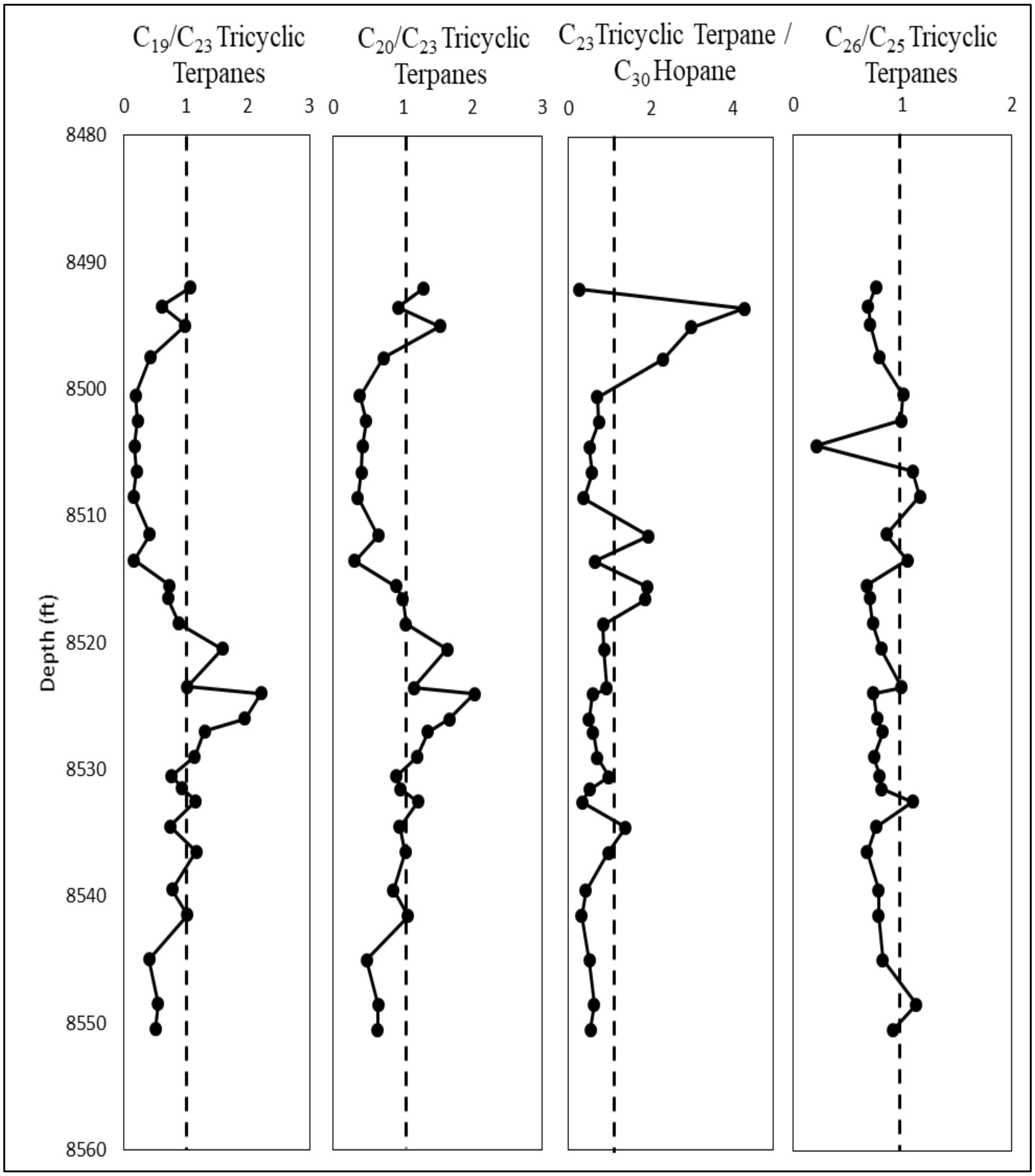


Figure 31. Previously discussed Tricyclic Terpane Ratios of the Kephart-I Well. Note the variations of the ratios through the core.

which periodically received a source contribution from higher plants. The C_{26}/C_{25} value of 0.83 also indicates a marine depositional environment with low salinity for the Kephart-I core (Tao et al., 2015). The absence, or very low concentration of gammacerane, a biomarker characteristic of hypersaline environments, in all of the samples also supports the fact that the Morrow is generally deposited under low salinity conditions.

The tricyclic terpane ratios for the two core samples from the Laverne-State-I well indicate that the terrestrial environment prevailed during the deposition of the Morrow Shale in Harper County. The abnormally high C_{19}/C_{23} and C_{20}/C_{23} ratios (average of 2.17 and 2.88; respectively) combined with very low C_{23}/C_{30} values (average of 0.05) suggest that the terrestrial higher plants were the major input of the organic matter during the deposition of the Morrow in Harper County.

4.3.4 The Pentacyclic Terpanes

The pentacyclic terpanes (hopanes; **VIII**) originate from prokaryotic organisms and higher plants (Ourisson et al., 1987). The bacterial organisms are the main source of hopanoids that produce hopanes (Ourisson et al., 1987). Since bacteria are ubiquitous in almost all oils and sedimentary rocks, they were proposed to be the most abundant source of organic matter on earth (Ourisson and Albrecht, 1992; Peters et al., 2005). The hopanes are a very useful biomarker group for making correlations and to assess the maturity, depositional environment, source input and biodegradation. They appear in the m/z 191 ion chromatogram together with the tricyclic and tetracyclic terpanes and can be identified using both GCMS and GCMS-MS.

The distribution of the pentacyclic hopanes in the Morrow Shale was identified from the m/z 191 chromatograms as shown in Figure 32 with the peak identifications given in Table 8. The most abundant compounds in the m/z 191 ion chromatograms are the C_{30} and C_{29} 17(α)-hopanes. The oils and sedimentary extracts with C_{29}/C_{30} 17(α)-hopane ratio greater than 1.0 are generally associated with anoxic carbonates, evaporites or marl source rocks (Connan et al., 1986). Riva et al. (1988) suggested that this ratio can be used as a scale for carbonate richness where ratios greater than one indicate an anoxic carbonate-rich depositional environment. Although none of the analyzed samples have C_{29}/C_{30} 17(α)-hopane ratio greater than 1.0, some of them (MOR-57, MOR-74, MOR-75) have significantly higher values than the others. The higher C_{29}/C_{30} 17(α)-hopane ratio in these samples may be related to an increase in carbonate content or evaporitic conditions prevailing during deposition. This interpretation for the MOR-57, MOR-75 samples is also supported with tricyclic terpane ratios as discussed in the previous part.

Another characteristic of the m/z 191 ion chromatograms for the Morrow samples is the low concentration of extended hopanes (C_{31}-C_{35}) compared to the C_{30} 17(α)-hopane. The C_{31} is the most dominant homohopane among the other extended hopanes and C_{35} is either absent or in very low concentration in the Morrow samples. The 22R and 22S configurations of the homohopanes are useful for maturity assessment. The 22R epimer is biologically derived and converted into 22S with the increasing maturity (Peters et al., 2005). In the Wang (1993) Morrow samples, the average C_{31} 22S/C_{31} (22S+22R) ratio is 0.53 while this ratio is 0.58 in the Kephart-I Well and 0.59 for the Laverne-State-I Well. According to Peters et al. (2005), the range between 0.50 and 0.54 indicates a very early

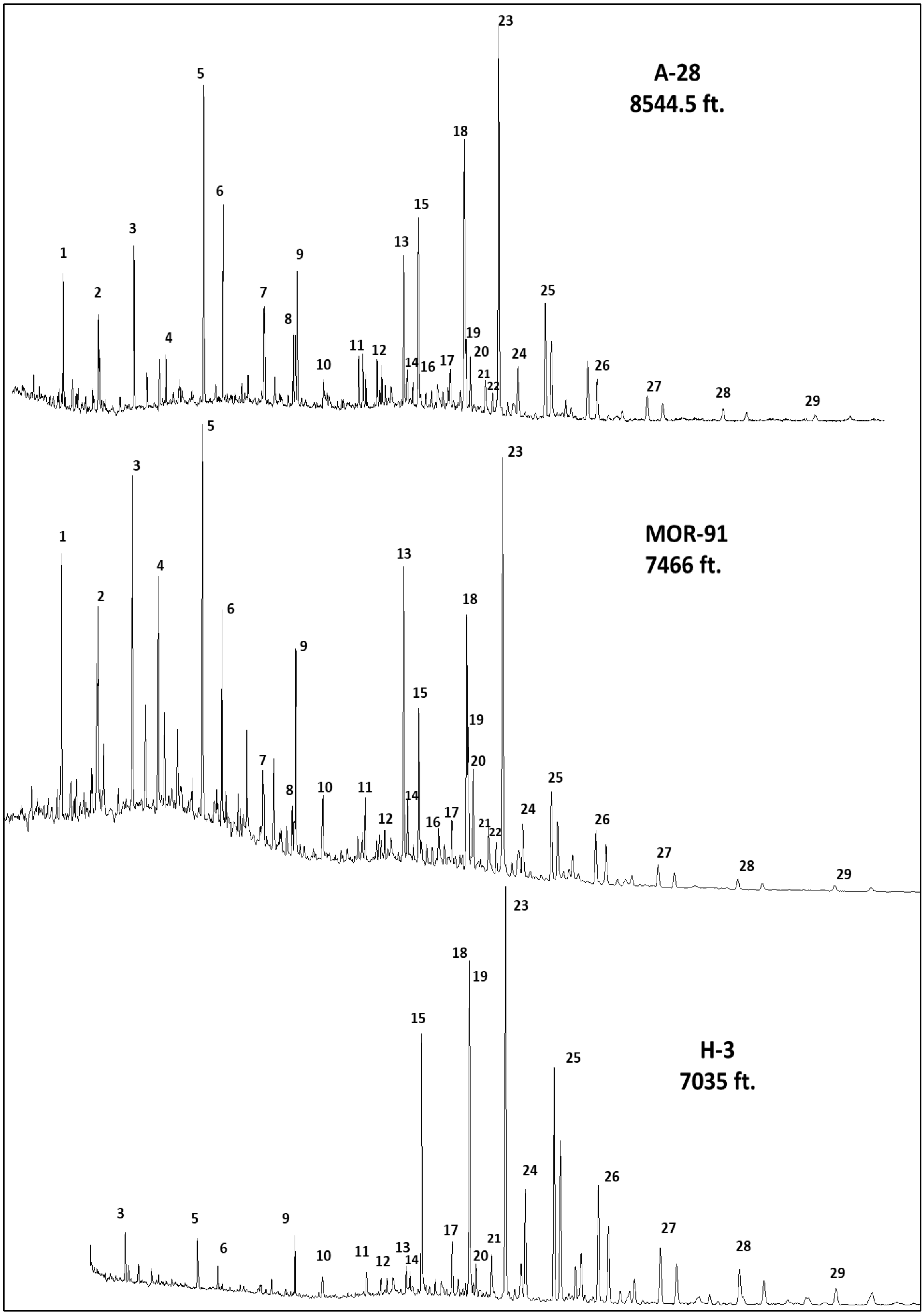
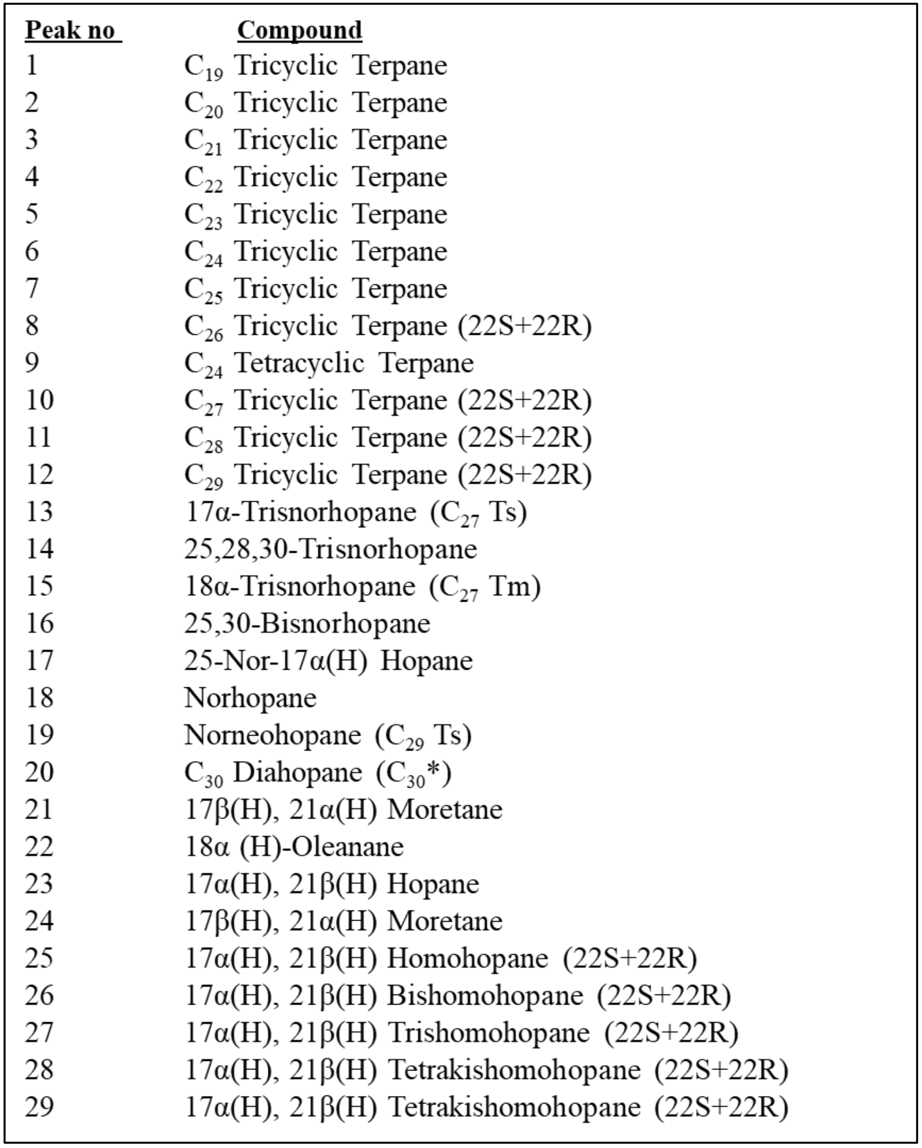


Figure 32. m/z 191 ion chromatogram showing the distribution of terpanes

Table 8. m/z 191 Terpane Compound Identification



Peak no	Compound
1	C_{19} Tricyclic Terpane
2	C_{20} Tricyclic Terpane
3	C_{21} Tricyclic Terpane
4	C_{22} Tricyclic Terpane
5	C_{23} Tricyclic Terpane
6	C_{24} Tricyclic Terpane
7	C_{25} Tricyclic Terpane
8	C_{26} Tricyclic Terpane (22S+22R)
9	C_{24} Tetracyclic Terpane
10	C_{27} Tricyclic Terpane (22S+22R)
11	C_{28} Tricyclic Terpane (22S+22R)
12	C_{29} Tricyclic Terpane (22S+22R)
13	17α-Trisnorhopane (C_{27} Ts)
14	25,28,30-Trisnorhopane
15	18α-Trisnorhopane (C_{27} Tm)
16	25,30-Bisnorhopane
17	25-Nor-17α(H) Hopane
18	Norhopane
19	Norneohopane (C_{29} Ts)
20	C_{30} Diahopane (C_{30}*)
21	17β(H), 21α(H) Moretane
22	18α (H)-Oleanane
23	17α(H), 21β(H) Hopane
24	17β(H), 21α(H) Moretane
25	17α(H), 21β(H) Homohopane (22S+22R)
26	17α(H), 21β(H) Bishomohopane (22S+22R)
27	17α(H), 21β(H) Trishomohopane (22S+22R)
28	17α(H), 21β(H) Tetrakishomohopane (22S+22R)
29	17α(H), 21β(H) Tetrakishomohopane (22S+22R)

oil window while the range between 0.57 and 0.62 indicates that late oil window. Moreover, in Kephart-I Well, this ratio shows little or no variation indicating that the thermal maturity does not fluctuate significantly through the core (Figure 33, Table 6).

The ratio of 18(α)-trisnorhopane(Ts;**IX**)/17(α)-trisnorhopane(Tm;**X**) or Ts/Ts+Tm provides another maturity assessment in the immature to postmature range. Ts is more stable than Tm thus the ratio is expected to increase with increasing maturity.

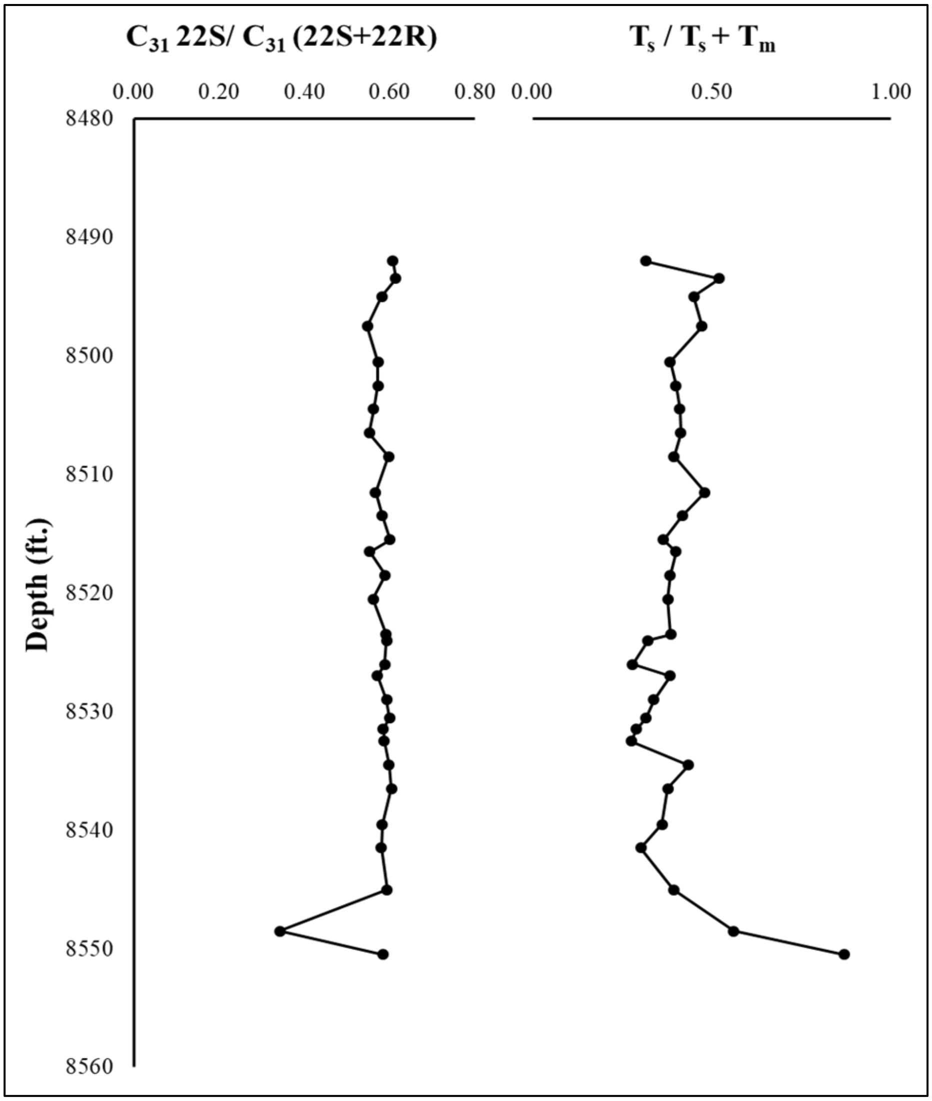


Figure 33. C_{31}22S/C_{31}(22S+22R) and T_s/T_s+T_m logs vs. depth showing the maturity variation through the Kephart-1 Well.

However, this ratio is highly dependent on the facies change and should only be used as a maturity indicator when the source rock is composed of consistent organic facies (Waples and Machihara, 1991). In the source rock samples from Wang (1993), the average Ts/Ts+Tm ratio is 0.5 ranging between 0.06 and 0.74. The results demonstrate that the maturity of the Morrow varies significantly in the Anadarko Basin as it was discussed above. In Kephart-I well, Ts/Ts+Tm ratio shows only slight variations until 8545 ft., and after that depth it shows a significant increasing compared to the C_{31} 22S/C_{31}

(22S+22R) plot. The increasing trend in the Ts/Ts+Tm plot might be related to a sudden increase in maturity although such an abrupt change in maturity in a 60 feet core is quite unexpected. It might also be related to facies change as Ts/Ts+Tm is highly susceptible to facies change and given the fact that the Morrow was deposited under highly variable, dynamic conditions might lead to different facies associations through the core.

4.3.4.1 Rearranged Hopanes

Another feature of the m/z 191 ion chromatograms is the relatively high concentration of rearranged hopanes such as 18(α)-30-norneohopane (**XI**) and 17(α)-diahopane (**XII**). The rearranged hopanes and the regular hopanes have identical carbon skeletons with different methyl side chain carbon positions (Peters and Moldowan, 1993). So far, there have been several studies conducted on the geochemical significance of 17(α)-diahopane, however its origin and geochemical significance is still disputed (Yang et al., 2016). For example, Moldowan et al. (1991a) suggested that the 17(α)-diahopanes resulted from the rearrangement of hopanoids with a functional group in the D-ring and share common structural features with C_{27}-C_{30} 17(α)-hopanes (Zhang et al., 2009). Peters et al. (2005) mentioned that 17(α)-diahopane and C_{27}-C_{30} 17(α)-hopanes originate from a common bacterial precursor. Philp and Gilbert (1986) suggested that they are associated with a terrestrial environment due to their occurrence in coals and oils derived from terrigenous source material. Alternatively, Zhang et al. (2009) proposed that this compound might be related to the red algae derived from a marine environment. The most consistent interpretation about the origin of the 17(α)-diahopane, however, is the fact that they are most probably derived from the rearrangement of hopanoids in clay rich environments under oxic conditions during diagenesis (Moldowan et al., 1991a; Yang et al., 2016). Jiang et al. (2018) mentioned that occurrence of the 18(α)-30-norneohopane and 17(α)-diahopane is mainly controlled by redox conditions of the depositional environment and salinity of the water. Anoxic conditions are the least favorable for their occurrence, while suboxic environments and brackish waters are the most favorable depositional conditions for their occurrence (Jiang et al., 2018). Besides its association with the depositional conditions, 17(α)-diahopane has been also associated with increasing thermal maturity (Kolaczkowska et al., 1990; Moldowan et al., 1991a). Horstad et al. (1990) suggested that 17(α)-diahopane is more stable than 18(α)-30-norneohopane and 17(α)-hopane and added that increasing maturity should result in an increase of the 17(α)-diahopane/(17(α)-diahopane+17(α)-hopane) ratio. However, it does not necessarily mean that all highly mature source rocks and oils will contain 17(α)-diahopane as its occurrence can be effected by various other geological factors (Yang et al., 2016).

Almost all of the samples in this study, with one exception, have relatively high concentrations of rearranged hopanes. Their relatively high abundance in the Morrow samples demonstrates that the Morrow was deposited under clay-rich hyposaline suboxic conditions. MOR-75 is the only sample with no 18(α)-30-norneohopane and the highest C_{29} hopane concentration among the other samples which may be related to an increase in carbonate content or evaporitic conditions prevailing during deposition.

4.3.4.2 Oleanane

One of the most interesting features of the m/z 191 ion chromatograms was the unusual occurrence of oleanane in the Morrow samples. 18α(H)-Oleanane (**XIII**) has been identified tentatively in most of the Wang (1993) source rocks and the Kephart-I core samples (Figure 34; Table 9).

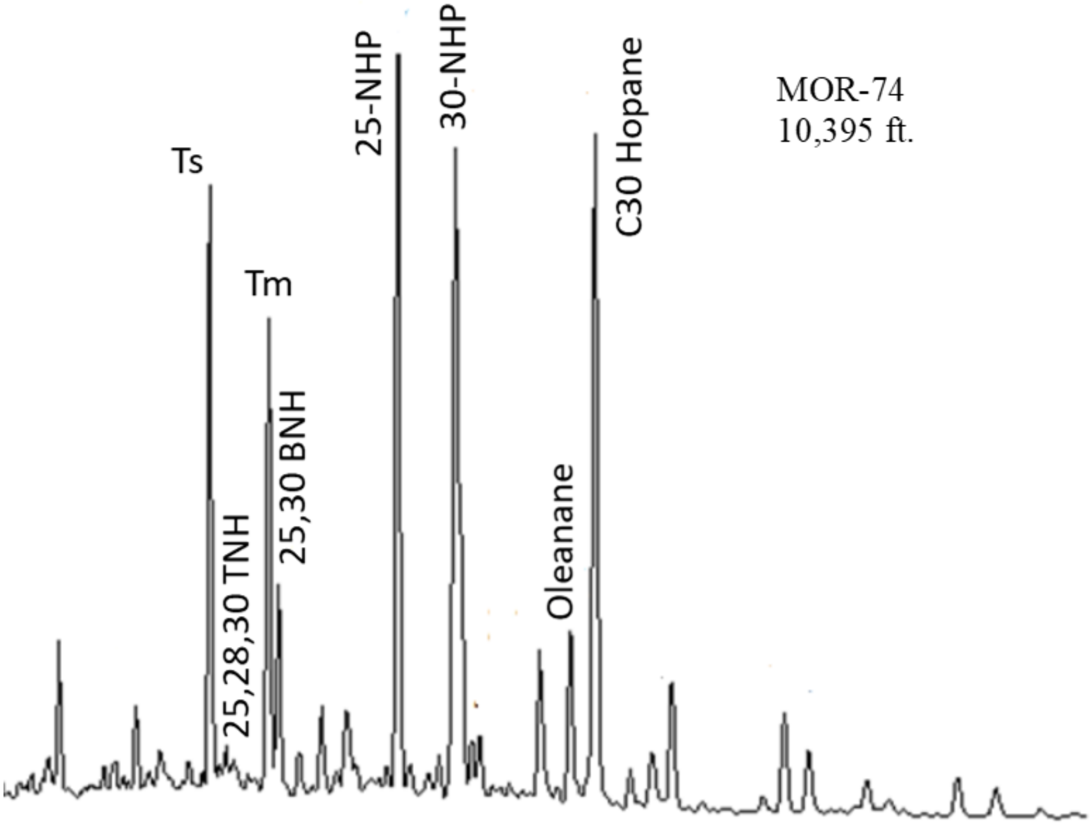


Figure 34. Representative m/z 191 pentacyclic terpane distribution of the Morrow sample

Oleanane is a pentacyclic triterpenoid derived by the alteration of the β-amyrin, derived from angiosperms (Armstroff et al., 2006; Udo and Ekweozor, 1990). The fossil records show that the angiosperms evolved and flourished in the early Cretaceous Period, which is why oleanane has been widely used as an age-specific biomarker for the Cretaceous and younger rocks and oils (Riva et al., 1988; Moldowan et al., 1994). However, the absence of oleanane does not necessarily mean that the petroleum was derived from the Lower Cretaceous or older source rocks as the depositional conditions play an important role in the preservation of oleanane (Al-Ameri et al., 2010).

Table 9. Calculated concentrations of 1,2,8-TMP, 1,2,7-TMN, oleanane, 25-NHP, 25,28,30-TNH, 25,30-BNH in Kephart-1 Well.

SAMPLE ID	1,2,8-TMP (mg/gTOC)	1,2,7-TMN (mg/gTOC)	Oleanane (µg/gTOC)	25-NHP (µg/gTOC)	25,28,30-TNH (µg/gTOC)	25,30-BNH (µg/gTOC)
A-1	5393.6	13605.3	0.0	0.0	2.5	1.4
A-2	43970.5	27598.0	6.75	10.72	4.33	17.61
A-3	55826.2	11737.7	6.0	12.2	0.0	0.0
A-4	35177.8	3258.9	5.20	14.48	2.94	12.98
A-5	11504.1	0.0	1.0	18.8	3.2	4.8
A-6	24606.7	2935.7	1.24	28.43	5.07	6.53
A-7	31558.9	20811.7	1.3	35.3	7.0	3.4
A-8	16609.2	4977.3	0.73	21.71	4.43	2.25
A-9	4474.5	841.1	0.7	16.2	3.1	2.6
A-10	20698.1	6832.3	2.11	11.98	2.61	9.58
A-11	11556.1	1267.4	1.0	57.4	11.7	8.5
A-12	30671.8	64251.6	9.30	21.28	3.54	34.04
A-13	7584.0	23717.6	2.7	7.1	1.8	9.1
A-14	5776.4	9675.7	7.91	21.07	2.23	32.78
A-15	8481.6	11696.9	6.8	9.1	1.8	14.1
A-16	10471.0	89042.1	14.57	19.52	4.59	31.32
A-17	4736.5	16186.8	3.1	6.2	1.0	9.3
A-18	6782.6	33264.7	2.30	4.56	1.41	8.98
A-19	9924.9	39177.8	1.3	6.0	2.9	6.3
A-20	4982.7	10612.9	2.28	3.28	1.44	5.76
A-21	4774.1	16728.2	1.9	4.5	1.4	7.8
A-22	2922.2	4729.9	1.65	3.78	2.91	7.21
A-23	19017.2	23403.0	4.4	10.2	10.5	25.2
A-24	10941.7	30993.2	10.04	10.52	1.86	17.25
A-25	10587.6	13170.6	3.7	7.7	2.3	17.2
A-26	8281.2	7052.1	1.26	4.30	3.57	6.25
A-27	8707.6	7139.1	0.9	2.2	1.9	5.3
A-28	10625.2	36114.4	6.30	10.84	2.53	19.60
A-29	3629.1	722.1	2.5	19.1	4.3	8.9
A-30	17091.7	5810.5	0.00	15.01	10.22	4.21

For instance, hypersaline conditions were suggested to minimize the diagenetic alteration of oleanane while freshwater conditions prompt the degradation and aromatization of the oleanane (McCaffrey et al., 1994; Murray et al., 1997a; Al-Ameri et al., 2010). Murray et al. (1997b) found that the diagenetic contact between oleanane and the seawater surface improves the hydrogenation and helps the preservation of oleanane. They further suggested that the deltaic environments influenced by marine waters during early diagenesis are the best preservation condition for oleanane and other related compounds (Murray et al., 1997a). This phenomena was also supported by the Peters et al. (2000) study in which the oleanane ratio in Mahakam Delta oils generally increased in an offshore direction rather than an onshore one.

Oleanane has two isomers as 18α(H)-oleanane and 18β(H)-oleanane (Figure 35; Riva et al., 1988; Mahmoodi and Bhattacharya 2013). The 18β(H)-oleanane co-elutes with 18α(H)-oleanane in conventional non-specialized gas chromatography thus their analytical separation is technically very difficult (Riva et al., 1988). The complete analytical separation of 18α(H)-oleanane and 18β(H)-oleanane was first achieved by Riva et al. (1988), who identified the latter occurred peak in the m/z 191 ion chromatogram as 18β(H)-oleanane. 18α(H)-oleanane is thermally more stable than the 18β(H)-oleanane and is the more predominant isomer in mature rock extracts and oils (Alberdi and López, 2000). The separation of 18α(H)-oleanane and 18β(H)-oleanane could not be achieved in this study because of the inadequate laboratory procedures or non-specialized gas chromatography, so only 18α(H)-oleanane isomer will be referred to in the remaining parts of the thesis.

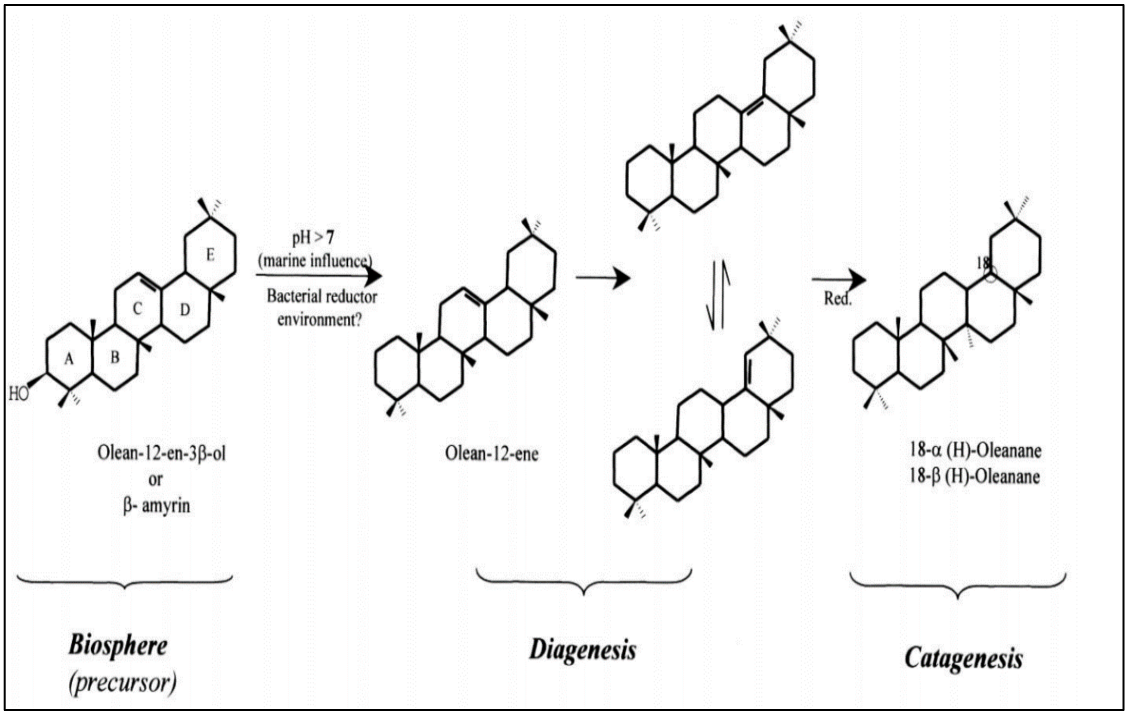


Figure 35. Scheme showing the diagenesis and early catagenesis and precursor relationship of oleanane (Alberdi and López, 2000)

Oleanane can be identified by using the m/z 191 and 412 ions when analyzing the saturate fractions of the rock extracts and oils (Alberdi and López, 2000; Nytoft et al., 2002). However, oleanane is susceptible to co-elution with another terpanes such as lupanes (**XIV**; Nytoft et al., 1997; Nytoft et al., 2002), some other C_{30} hopanes and demethylated hopanes of 25-nor-17a-(H)-hopane in m/z 191 and 412 chromatograms (Alberdi and López, 2000). In order to eliminate this possibility, it is essential to use GC-MS-MS in order to see the parent daughter relationship. For instance, m/z 412 to 191 parent-daughter transition corresponds to the potential occurrence of both oleanane and lupane, while m/z 412 to 369 parent-daughter transition can only be attributed to the presence of lupane as oleanane does not have an adequate sidechain and hence does not produce the m/z 369 fragment (Figure 36; Nytoft et al., 2002). In this study, the presence

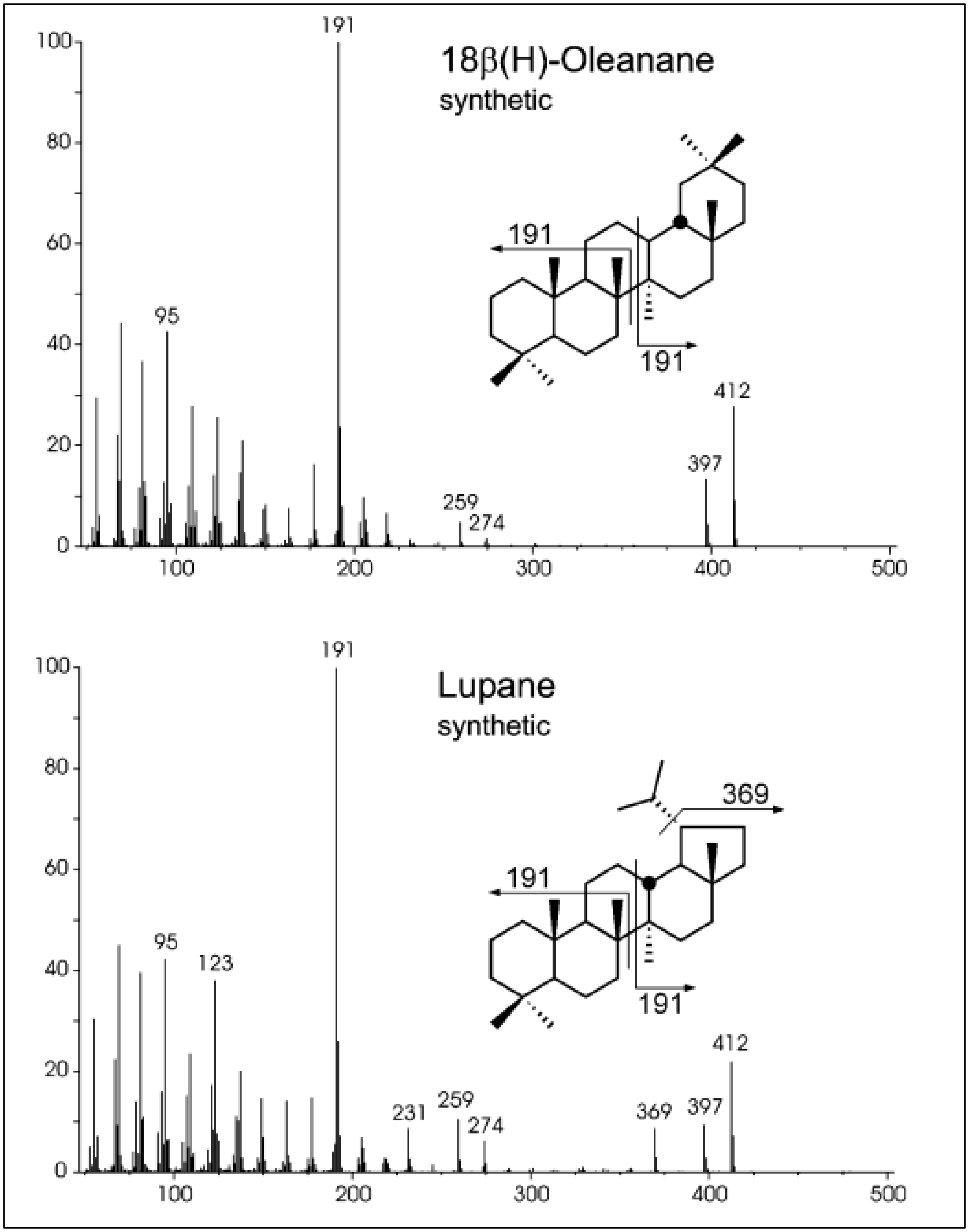


Figure 36. Mass spectra of lupane and oleanane, their structures and fragmentation patterns (Nytoft et al. 2002). Note that both of the compounds have very similar chemical structure and mass spectra and lupane differs from 18α(H)-oleanane with the presence of m/z 369 fragment.

of 18α(H)-oleanane was determined by GC-MS-MS and monitoring the m/z 412 to 191 and 412 to 369 parent-daughter transitions (Figure 37). M/z 412 to 369 parent-daughter transition of the GC-MS-MS, tentatively confirms the presence of lupane in the Morrow source rocks. However, the presence of lupane does not necessarily mean that oleanane is absent in these samples since oleanane and lupane are two structurally related compounds that are proposed to be produced by angiosperms (Nytoft et al., 2002) and are expected to occur together in the rock extracts. The peak height ratios of the lupane/hopane (in m/z 412 to 369) and (oleanane + lupane)/hopane (in m/z 412 to 191) in GC-MS-MS are calculated as 0.25 and 0.44; respectively in MOR-74 source rock sample. The results confirm the tentative presence of the 18α(H)-oleanane in the Morrow source rocks and might suggest that “the peak” is comprised of 18α(H)-oleanane and lupane in varying proportions.

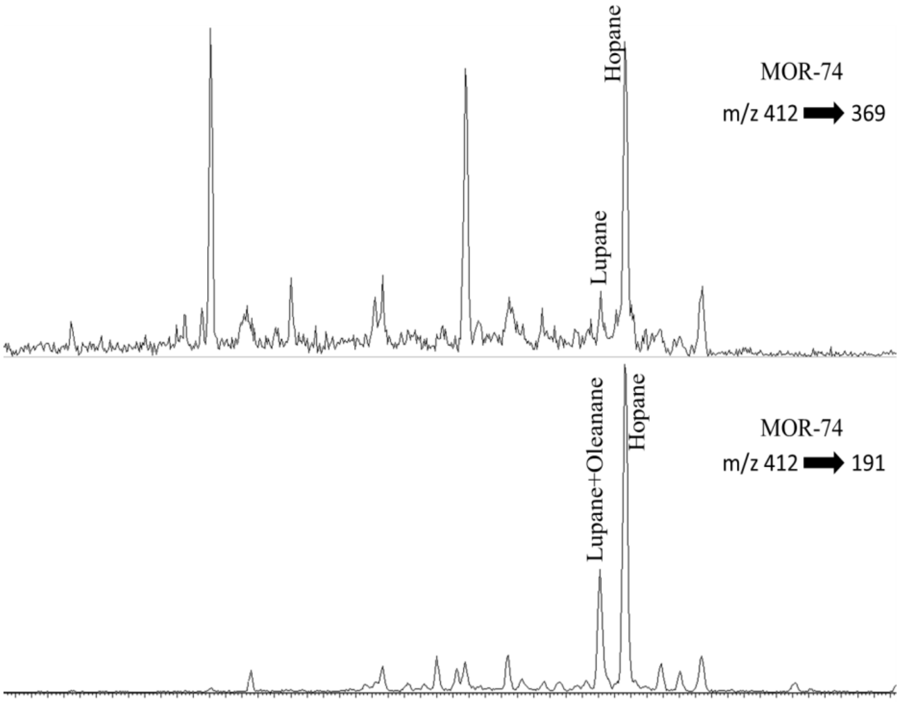


Figure 37. GCMS-MS transitions of m/z 412 to 369 and m/z 412 to 191 showing the presence of the lupane and oleanane (see discussion above) in the Morrow samples

Although the presence of 18α(H)-oleanane in pre-Cretaceous source rock samples is unusual, there have been other studies that confirmed the presence of 18α(H)-oleanane in pre-Cretaceous rocks. For instance, Wood confirmed the tentative presence of 18α(H)-oleanane in the Chesterian Limestone in the Anadarko Basin in his unpublished MS thesis (2017). Moldowan et al. (1994) identified 18α(H)-oleanane in both Middle Jurassic marine siltstones of Tyumen Formation from West Siberia, Russia and in a Pennsylvanian coal ball from Illinois, USA. Peters et al. (1999) identified 18α(H)-oleanane in a Middle Jurassic Brora coal in Scotland. Moreover, Taylor et al. (2006) identified 18α(H)-oleanane in the Upper Permian rock extracts from Guizhou Province, China. These tentative identifications of 18α(H)-oleanane even in low concentrations clearly show that the presence of 18α(H)-oleanane is not indisputable evidence for the Cretaceous or younger aged source rocks and oils (Peters et al., 1999).

In this study, the tentative presence of 18α(H)-oleanane has also been identified in several of the Wang (1993) samples and Kephart-I core samples. There are few possible explanations in the literature for the unexpected occurrence of 18α(H)-oleanane in the pre-Cretaceous sediments. Taylor et al. (2006) developed a method that uses zeolite in order to eliminate the potential co-elution of hopanes with the oleanane and then confirmed the presence of 18α(H)-oleanane in non-angiosperm seed plant fossils of Cretaceous Bennettitales and the Permian Gigantoptridales. Since these non-angiosperm seed plants share significant common characteristics with the angiosperms, they have been suggested to be a sister group, or a member of the angiosperms (Taylor et al., 2006). The results of the Taylor et al. (2006) study indicates that the oleanane identified in this and previously mentioned studies could have originated from the non-angiosperm seed plants that evolved during the Late Paleozoic, suggesting a different plant group as a precursor of oleanane. Nevertheless, the other possible explanation is that angiosperms could have evolved from other seed plant lineages long before the Early Cretaceous (Taylor et al., 2006).

Molecular phylogeny analysis has been widely used to observe molecular differences in DNA sequences and to assess the organism's evolutionary pathway. Increasing availability of the molecular data has aided several attempts to make the age estimate of angiosperms by use of molecular clock analysis. However, most of the authors proposed different age estimates for evolution of the angiosperms while several of them have agreed that the earliest form of the angiosperms should have occurred long before Cretaceous time (Ramshaw et al., 1972; Brandl et al., 1992; Smith et al., 2011; Magallón et al., 2013). For instance, Ramshaw et al. (1972) utilized a protein sequence of a plant mitochondria and used it to determine the age of angiosperms. As a result, Ramshaw et al. (1972) suggested that the molecular age of the angiosperms is several geological periods before the Cretaceous Period (520-400 Mya). Moreover, Martin et al. (1989) used the glycolytic enzyme of glyceraldehyde 3-phosphate dehydrogenase (GAPDH) in the angiosperm plants to estimate the age when this enzyme was first synthesized by the organisms (Friis et al., 2011). The results were supportive of the work of Ramshaw et al. (1972) with the estimated molecular age determination of ~ 319 Mya ±33 Mya. (Friis et al., 2011). In conclusion, several molecular phylogeny studies support an earlier evolution for the angiosperms reaching back to the Early Carboniferous. These studies suggest that the oleanane found in the pre-Cretaceous rocks, including this study, may be derived from the earliest angiosperms which evolved long before the Cretaceous and/or originated from non-angiosperm seed plants that share significant common characteristics with the angiosperms. Another possible explanation of the tentative presence of oleanane in pre-Cretaceous rocks may be a different plant group as a precursor for oleanane. However, this explanation is quite unlikely due to the lack of evidence in the literature that relates any other plant group with oleanane.

4.3.4.3 Demethylated Hopanes

Demethylated hopanes occur as a series of C_{27} – C_{35} hopanes that structurally differ from the hopanes with the absence of methyl group at the A/B ring (Rullkötter and Wendisch, 1982; Volkman et al., 1983). They can be identified in both m/z 171 and m/z 191 ions of the saturate fractions. The demethylated hopanes are formed from the bacterial transformation of the hopanes and they are widely associated with the heavy biodegradation (Volkman et al., 1983). They are commonly found in the biodegraded oils and their presence in the rock extracts is unusual as they are not observed in the pyrolysis products of the kerogen or asphaltene (Noble et al., 1985). However, this study confirms the tentative presence of demethylated hopanes (such as 25-norhopanes (NHP; **XV**), 25,28,30-trisnorhopane (TNH; **XVI**), 25,30-bisnorhopane (BNH; **XVII**) in multiple source rock samples (Figure 38). Identifying demethylated hopanes in the Morrow rock extracts was somewhat surprising. However, there are several other studies that reported the presence of demethylated hopanes in source rock extracts. Curiale et al. (1985) identified high concentrations of 25-NHP and 25,28,30 TNH in the Monterey rock extracts and in certain San Joaquin Basin oils and extracts. Noble et al. (1985) identified 25,28,30 TNH, 25,30-BNH and 25-NHP in the Australian shales and noted that they are not present in the laboratory pyrolysates products of the extracted sediments. This suggests that the demethylated hopanes are not bounded to kerogen and should be present in the sediments as free hydrocarbon as they are not produced by thermal breakdown of the kerogen. In other words, the demethylated hopanes are allocthonous and their presence in the Australian Shales was related to either paleo-seepage of a heavily biodegraded oil into the source rock or biodegradation of the *in-situ* petroleum that might be trapped in the fractures of the shales during migration (Noble et al., 1985).

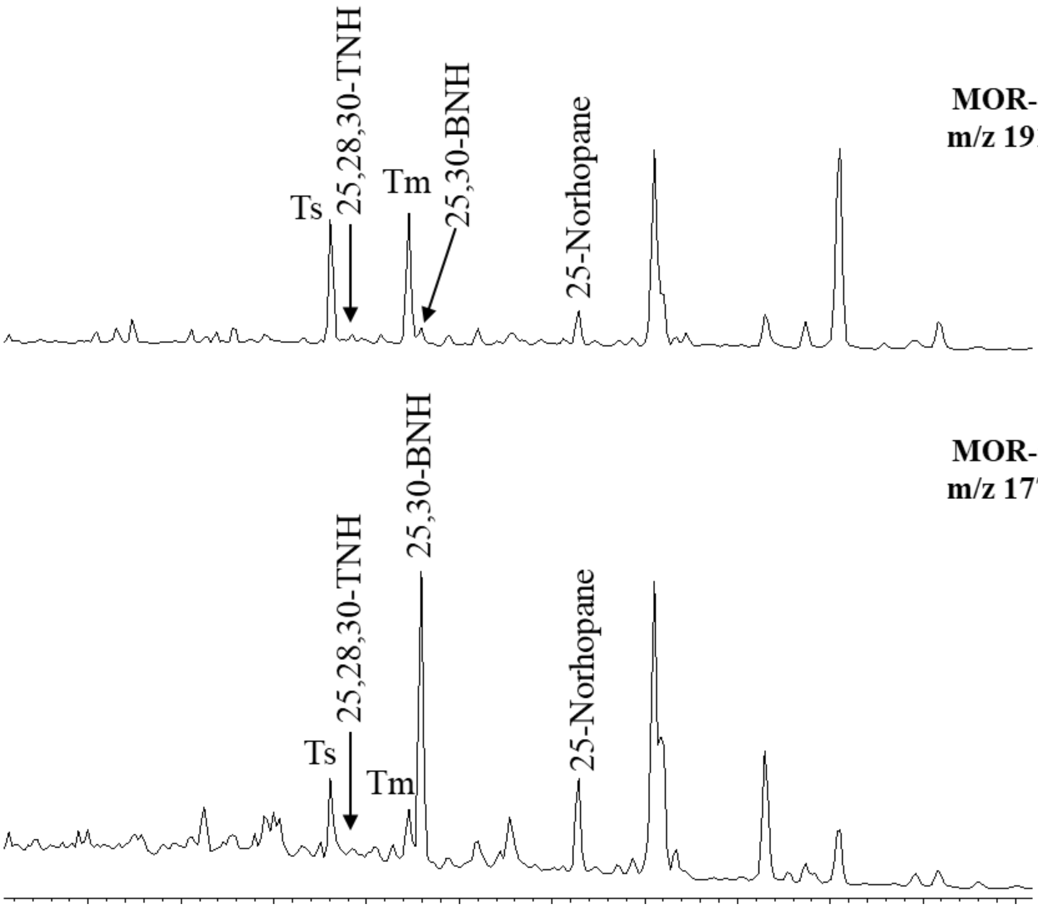


Figure 38. M/z 191 and m/z 177 ion chromatograms showing the identifications of the 25,28,30 TNH, 25,30 BNH and 25-norhopane.

The origin of the 25-norhopanes and its high concentration in heavily biodegraded oils have been a controversial issue for several decades (Moldowan and McCaffrey, 1995). There are three main hypotheses for the origin of the 25-norhopanes: I) They are produced as a result of microbial degradation but they are masked by the hopanes. They become enriched with the increasing biodegradation as the hopanes are removed. II) They originate from the demethylation of hopanes by the removal of the methyl group at C-10 in the hopane structure. III) They are not degradation products of hopanes but the microorganisms produce 25-norhopanes (Peters et al., 2005). As this compound is closely associated with reservoir biodegradation, its occurrence in the source rock extracts is unexpected. Blanc and Connan (1992) identified 25-NHPs in several rock samples and proposed that 25-NHPs are more likely to occur in marine and lacustrine source rocks that are deposited under dysoxic and hypersaline conditions. Philp (1983) proposed that 25-NHP might be deriving from specific source beds and not necessarily associated with biodegradation since they are not readily present in some heavily biodegraded oils.

The concentration of the demethylated hopanes vs. depth in Kephart-1 Well is presented in Figure 39, and the corresponding calculated concentrations are given in Table 9. The plot demonstrates that the demethylated hopanes show similar variations through the core indicating that they were most likely derived by the same mechanism. The tentative presence of the 25-NHP, 25,28,30-TNH, 25,30-BNH in the Pennsylvanian Morrow Shales might be explained by several mechanisms. Since they are not found in the pyrolysates of the Australian source rocks (Noble et al., 1985) and are abundant in biodegraded oils, their presence in the Morrow rocks might be related to sedimentary re-working. For instance, heavily biodegraded hydrocarbons such as tar-sands or asphalt deposits from an ancient reservoir could have been transported and entered into the Morrow source rocks at the time of deposition (Noble et al., 1985). Alternatively, oil could have migrated from an ancient reservoir but was trapped in the cracks of the

Morrow source rocks and biodegraded *in-situ* (Noble et al., 1985). Finally, as Peters et al. (2005) suggested, their presence could be also related to a very uncommon bacterial reworking of the organic matter.

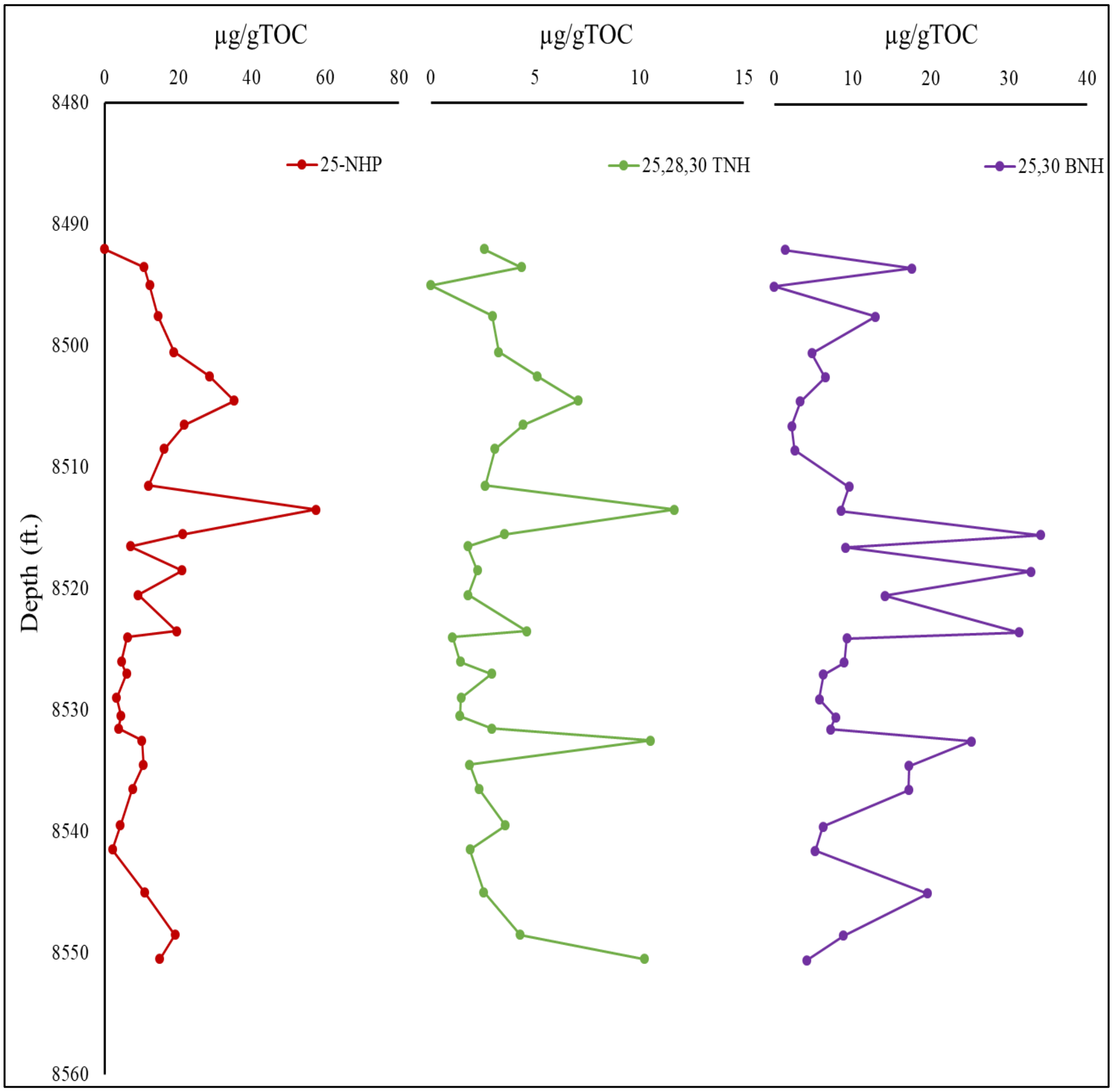


Figure 39. The cross plot of demethylated hopane concentrations vs. depth in the Kephart-1 Well

4.3.5 Steranes

Steranes in the Morrow source rock samples were identified in the m/z 217 ion chromatogram as shown in Figure 40 with peak identifications given in Table 10.

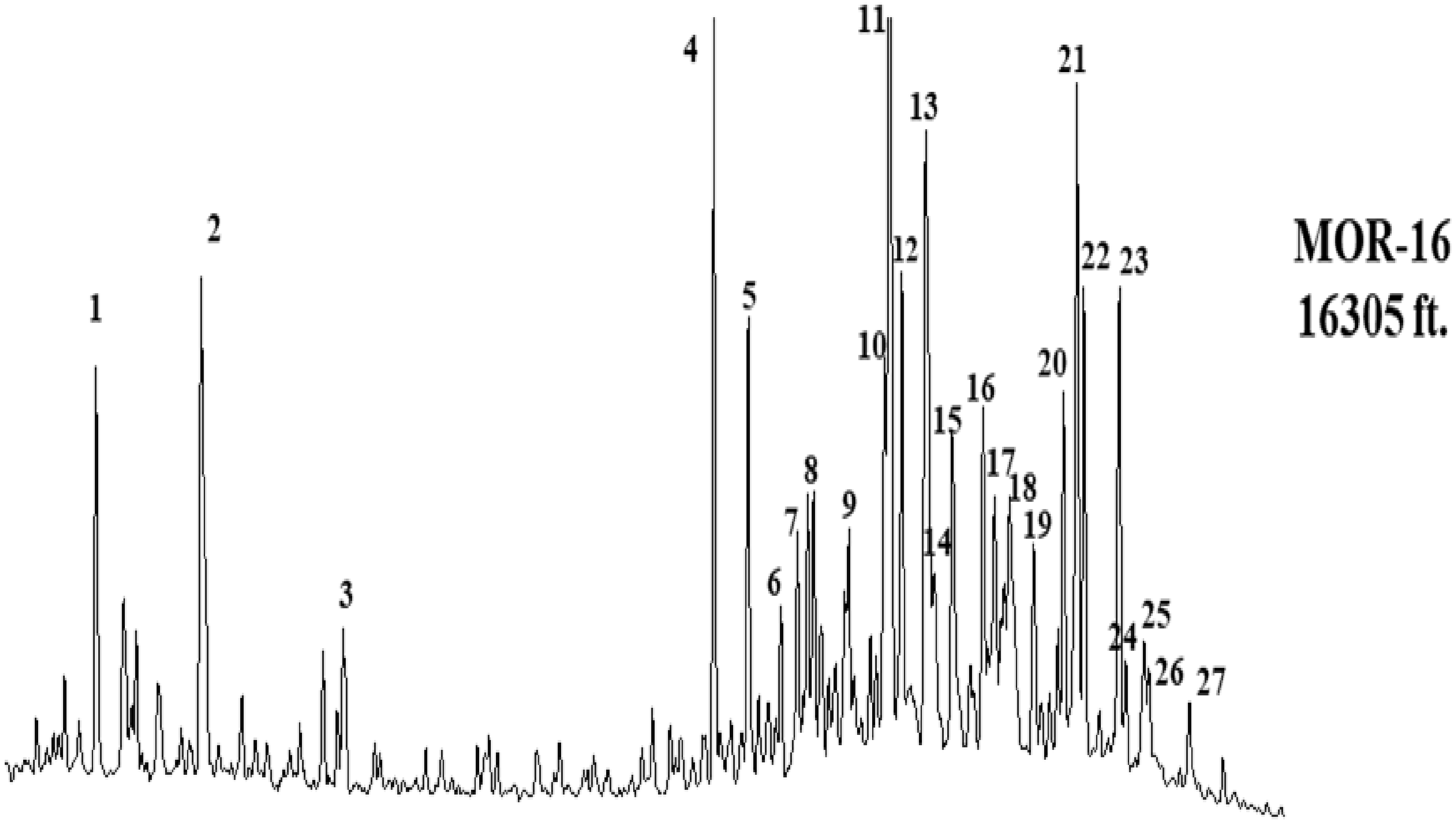


Figure 40. Partial fragmentogram of the m/z 217 showing sterane distribution

Table 10. Sterane compound identification in the m/z 217 chromatogram

Peak No	Compound
1	Diapregnane
2	5α(H), 14α(H), 17β(H) Pregnane
3	5α(H), 14α(H), 17β(H) Homopregnane
4	13β(H), 17α(H) Diasterane (20S)
5	13β(H), 17α(H) Diasterane (20R)
6	13α(H), 17β(H) Diasterane (20S)
7	13α(H), 17β(H) Diasterane (20R)
8	24-methyl- 13β(H), 17α(H) Diasterane (20S)
9	24-methyl- 13β(H), 17α(H) Diasterane (20R)
10	5α(H), 14α(H), 17α(H) Cholestane (20S) +C_{28} 24-methyl- 13α(H), 17β(H) Diasterane (20S)
11	5α(H), 14β(H), 17β(H) Cholestane (20R) + C29 24-ethyl- 13β(H), 17α(H) Diasterane (20S)
12	5α(H), 14β(H), 17β(H) Cholestane (20S) +C_{28} 24-methyl- 13α(H), 17β(H) Diasterane (20R)
13	5α(H), 14α(H), 17α(H) Cholestane (20R)
14	24-ethyl- 13β(H), 17α(H) Diasterane (20R)
15	24-ethyl- 13α(H), 17β(H) Diasterane (20S) + C30 24-propyl- 13β(H), 17α(H) Diasterane (20S)
16	24-methyl- 5α(H), 14α(H), 17α(H) Ergostane (20S) + C29 24-ethyl- 13α(H), 17β(H) Diasterane (20R)
17	24-methyl- 5α(H), 14β(H), 17β(H) Ergostane (20R)
18	24-methyl- 5α(H), 14β(H), 17β(H) Ergostane (20S)
19	24-methyl- 5α(H), 14α(H), 17α(H) Ergostane (20R)
20	24-ethyl- 5α(H), 14α(H), 17α(H) Stigmastane (20S)
21	24-ethyl- 5α(H), 14β(H), 17β(H) Stigmastane (20R) + C30 24-propyl- 13α(H), 17β(H) Diasterane (20R)
22	24-ethyl- 5α(H), 14β(H), 17β(H) Stigmastane (20S)
23	24-ethyl- 5α(H), 14α(H), 17α(H) Stigmastane (20R)
24	24-propyl- 5α(H), 14α(H), 17α(H) Cholestane (20S)
25	24-propyl- 5α(H), 14β(H), 17β(H) Cholestane (20R)
26	24-propyl- 5α(H), 14β(H), 17β(H) Cholestane (20S)
27	24-propyl- 5α(H), 14α(H), 17α(H) Cholestane (20R)

4.3.5.1 Steranes as Indicators of Depositional Environment and Organic Facies

Steranes are derived from sterols which are produced by higher plants, animals, algae and occasionally by prokaryotic organisms (Waples and Machihara, 1991). There are four main families of sterols with 27, 28, 29 or 30 carbon atoms that are converted into regular steranes by diagenetic alteration. Huang and Meinschein (1979) originally proposed that each ecological system has its own specific sterol contributions from biological sources therefore C_{27}, C_{28} and C_{29} sterol homologs derived from different organisms can be used to differentiate depositional environments by use of a ternary diagram. The authors also suggested that the same approach with steranes can also provide valuable paleoenvironmental information.

For instance, C_{27} steranes (or sterols; **XVIII**) are associated with marine phytoplankton and are indicators of red algae. C_{28} steranes (or sterols; **XIX**) are relatively more dominant in lacustrine green algae, while C_{29} steranes (or sterols; **XX**) might indicate terrestrial higher plants and brown and green algae (Huang and Meinschein, 1979; Moldowan et al., 1985; Volkman 1986; Volkman, 2003; Schwark and Empt, 2006). However, using the abundance of regular steranes on a ternary diagram to differentiate depositional environments has met with only limited success since steranes lose most of their specificity during their conversion from sterols (Volkman 1986). Nevertheless, Peters et al. (2005) suggested that the ternary diagram of the C_{27}, C_{28} and C_{29} regular steranes is useful to differentiate not only different groups of oils from different source rocks but also different organic facies of the same source rock. The ternary diagram of the regular steranes in the Morrow Shales is presented in Figure 41 and the corresponding values are shown in Table 11. It illustrates that the Morrow samples plot within a dispersed area but tend to generally fall between the estuarine to marine environments which supports the geological interpretation proposed for the Morrow

In general, the Morrow source rock samples from the Wang (1993) study and Laverne-State-I core samples are characterized by relatively higher concentrations of the C_{27} regular steranes compared to the C_{28} and C_{29} steranes indicating the dominance of the marine organic matter contribution. However, MOR-11, MOR-39, MOR-41 and MOR-75 samples, which are from different areas of the basin, are mainly dominated with C_{29} steranes indicating that the terrestrial higher plant input might be more dominant during deposition in these regions as it is also supported by the high C_{19} and C_{20} tricyclic terpane concentrations relative to C_{23}. The Kephart-I Well is mainly dominated by C_{29} regular steranes which might indicate either terrestrial higher plant contribution was dominant in this region or brown and/or green algae contribution into the depositional environment. Furthermore, the presence of C_{30} steranes (**XXI**), such as 24-*n*-propylcholestanes derived from Chrysophyte algae (Moldowan et al., 1990), in most of the studied samples confirms the marine input to the depositional environment. Hays et al. (2012) proposed that a C_{30} sterane index (C_{30}/C_{27}-C_{30} steranes) > 4% indicates a significant marine contribution to the organic matter. In the Wang (1993) source rock samples, the average C_{30} sterane index is 4% that ranges between 2%-6% while in Kephart-I Well the average C_{30} sterane index is 19%. The C_{30} sterane index for the H-2 and H-3 samples from Laverne-State-I Well are

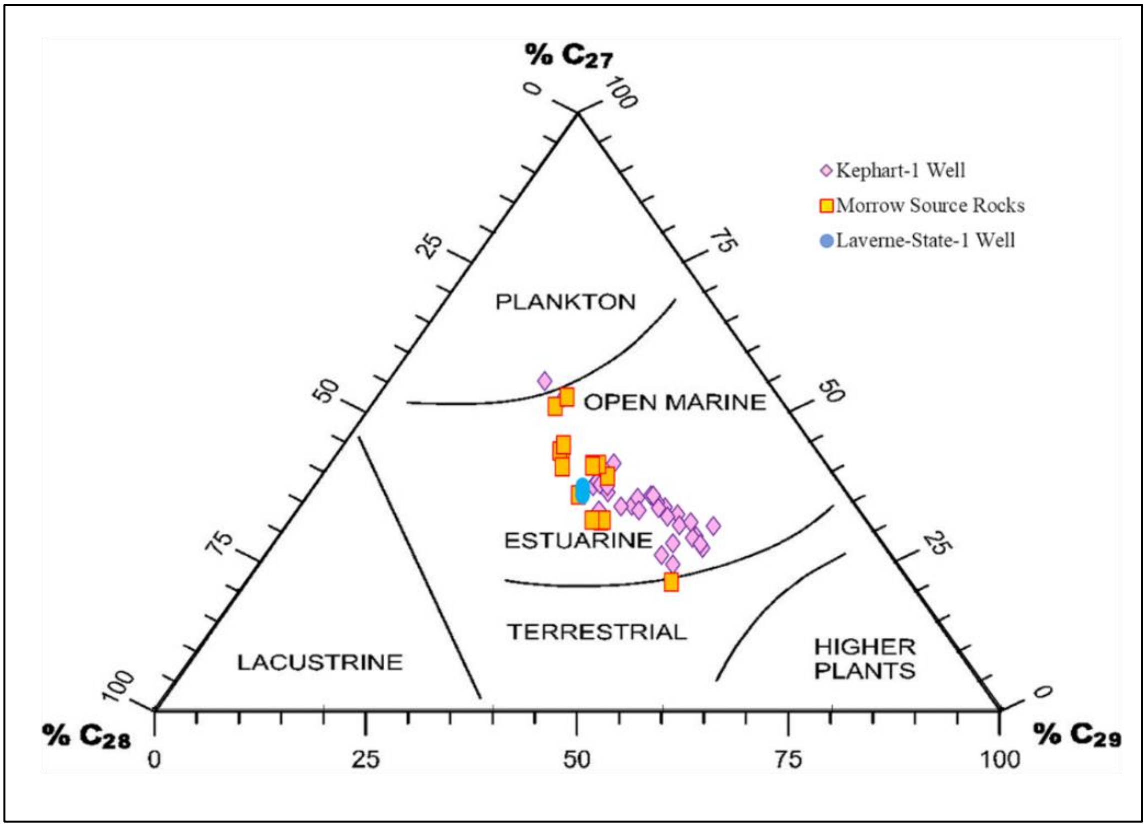


Figure 41. Steranes ternary diagram of the Morrow Shale samples (Modified after Shanmugam, 1985)

Table 11. Calculated sterane and diasterane ratios using peak areas for the Morrow samples

Samples	C_{27} Regular Steranes (%)	C_{28} Regular Steranes (%)	C_{29} Regular Steranes (%)	$\sum C_{30}/\sum C_{27}-C_{30}$	$\sum C_{27}$ Diasteranes/ $\sum C_{27}$ Regular Steranes	$\sum C_{21}-C_{22}/\sum$Steranes	$C_{29}\alpha\alpha\alpha S/C_{29}(\alpha\alpha\alpha S+\alpha\alpha\alpha R)$
A-1	34.1	26.6	39.3	0.0	0.2	0.1	0.4
A-2	30.8	18.7	50.60	0.00	1.07	0.80	0.09
A-3	34.0	22.7	43.3	0.2	0.9	1.0	0.1
A-4	35.9	23.5	40.60	0.25	0.76	0.59	0.22
A-5	37.5	29.5	33.1	0.4	0.5	0.2	0.3
A-6	38.3	28.6	33.10	0.38	0.47	0.22	0.36
A-7	37.7	28.5	33.7	0.4	0.4	0.2	0.4
A-8	33.3	30.9	35.79	0.44	0.57	0.18	0.40
A-9	36.5	28.3	35.3	0.4	0.5	0.1	0.4
A-10	41.2	25.2	33.61	0.32	0.66	0.64	0.29
A-11	37.4	27.8	34.8	0.4	0.5	0.2	0.4
A-12	34.7	23.3	42.01	0.22	0.84	1.17	0.22
A-13	33.8	23.6	42.6	0.2	0.8	0.7	0.2
A-14	35.5	25.2	39.29	0.38	0.76	0.47	0.19
A-15	32.8	21.9	45.4	0.2	0.8	0.4	0.2
A-16	32.3	23.3	44.39	0.24	0.84	0.48	0.17
A-17	29.1	21.5	49.4	0.1	0.7	0.4	0.2
A-18	27.1	21.8	51.14	0.15	0.72	0.29	0.14
A-19	34.1	27.9	38.0	0.2	1.0	0.3	0.2
A-20	28.7	22.1	49.18	0.17	0.73	0.35	0.16
A-21	27.7	21.7	50.6	0.2	0.7	0.4	0.1
A-22	24.3	26.7	49.03	0.08	0.66	0.20	0.27
A-23	25.9	27.2	46.9	0.2	0.4	0.1	0.3
A-24	35.9	23.2	40.96	0.24	0.77	0.45	0.15
A-25	30.8	22.6	46.5	0.1	0.8	0.4	0.2
A-26	33.4	26.1	40.49	0.11	0.50	0.26	0.31
A-27	27.8	24.9	47.3	0.1	0.5	0.2	0.3
A-28	31.4	21.0	47.61	0.20	0.84	0.19	0.13
A-29	52.4	25.5	22.1	0.2	1.0	0.2	0.3
A-30	55.1	26.4	18.50	0.19	0.84	0.15	0.38
H-2	37.4	30.8	31.8	0.2	0.1	0.0	0.4
H-3	36.1	31.5	32.39	0.09	0.25	0.10	0.42
MOR 57	42.1	30.9	27.0	0.1	1.2	0.3	0.4
MOR 33	43.5	30.5	26.07	0.05	0.74	0.31	0.34
MOR 2	36.1	32.0	32.0	0.0	1.2	0.4	0.5
MOR 74	40.7	31.6	27.72	0.05	1.32	0.54	0.37
MOR 91	39.2	26.9	33.9	0.0	1.0	1.0	0.3
MOR 75	21.4	28.3	50.22	0.03	0.42	0.27	0.42
MOR 41	31.7	31.4	36.9	0.0	0.7	0.4	0.4
MOR 11	31.8	31.2	37.03	0.05	0.56	0.15	0.35
MOR 39	31.8	32.5	35.7	0.0	0.7	0.5	0.4
MOR 64	51.0	27.3	21.77	0.03	0.85	0.20	0.38
MOR 43	41.2	27.7	31.1	0.1	0.6	0.1	0.3
MOR 66	52.5	25.1	22.38	0.03	0.78	0.14	0.35
MOR 86	41.1	27.1	31.8	0.0	0.5	0.2	0.5
MOR 16	40.9	27.9	31.21	0.06	0.55	0.17	0.38
MOR 68	44.5	29.6	26.0	0.0	1.0	0.2	0.3

15% and 9%, respectively (Table 11). The high C_{29} sterane concentrations and C_{30} sterane index values of the samples suggest that the Morrow source rocks are composed of mixed types of organic matter with terrestrial organic matter being the more dominant.

4.3.5.2 Steranes as Maturity Indicators

Waples and Machihara (1991) suggested that 20R and 20S epimers of the steranes provide a very important maturity assessment among the other biomarkers. The ratios of both 20S/20R and 20S/20S+20R gives highly specific results for the extent of maturity ranging from immature to mature rocks (Peters et al., 2005). It was proposed that the ααα form of the 20 R configuration is the biologically derived form of the steranes and with increasing maturity, 20R configuration decomposes with increasing 20S concentration (Waples and Machihara, 1991). Figure 42 shows the C_{29} (20αααS/20αααS+20αααR) steranes variations with the depth. However, the data shows scattered distribution with no specific maturity trend. There might be possible explanations of the scattered C_{29} (20αααS/20αααS+20αααR) data. To begin with, as previously discussed, the Morrow can be composed of different lithofacies even over short distances, which might result in such a scattered maturity graph. Secondly, the presence of demethylated hopanes in the Morrow suggests possible paleo-seepage from an ancient reservoir as discussed above. Re-working of organic matter from more mature ancient rock might result in such a scattered maturity log plot. Finally, oil staining from drilling additives can be another reason as previously discussed in Chapter 4.1 (Waples and Machihara, 1991; Peters et al., 2005).

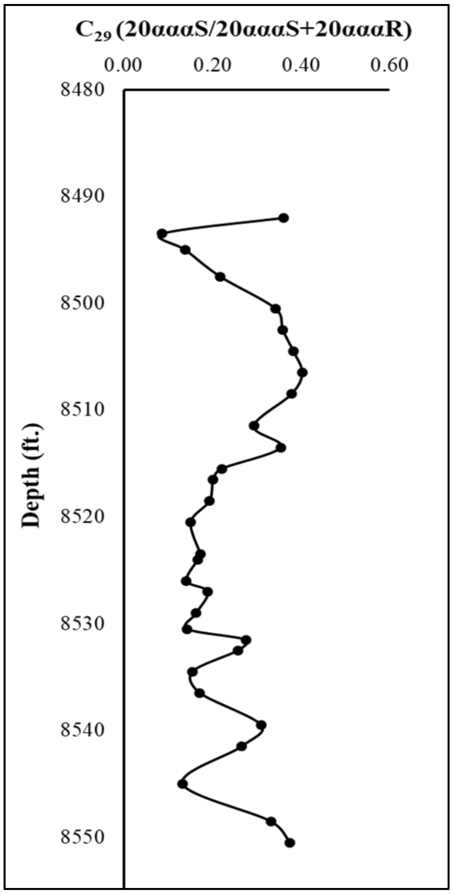


Figure 42. C_{29}(20αααS/20αααS+20αααR) vs. depth showing the maturity variation through the Kephart-1 Well

The C_{21} and C_{22} short chain steranes, namely pregnanes (**XXII)** and homopregnanes (**XXIII**) have been identified in relatively high concentrations in the Morrow source rock samples. ten Haven et al. (1985) identified high concentrations of these compounds in the hydrocarbons originating from gypsum samples from the northern Apennines basin in Italy and proposed that these biomarkers could be used as a characteristic for hypersaline environments. Wang et al. (2015) more recently proposed a valuable approach in which the occurrence of pregnane and homopregnane can indicate redox conditions, facies and mineral content of the source rock when combined with regular steranes and diasteranes ratios. For example, the samples with high diasteranes and low pregnanes are associated with the increasing oxic conditions, significant terrigenous input, high clay content, and organic lean carbonate rocks (Wang et al., 2015). The samples with low diasteranes and high pregnanes are associated with clastic starved, low Eh-high pH, sulfur-rich reducing depositional environments with low or no terrigenous input (Wang et al., 2015). Based on this approach, the Morrow source rock samples were plotted on the cross plot of $\sum C_{21-22}/\sum C_{27-29}$ Steranes vs. $\sum C_{27}$ diasteranes /regular C_{27} steranes (Figure 43; Table 11). The samples fell in a zone that is between the clay and carbonate rich source rocks. Wang et al. (2015) defined this zone as the ‘‘overlap zone, which should be considered as a mixed type of source rock comprised of comparable carbonate and clay mineral contents such as marls”. Thus, the lithology of the Morrow samples can be interpreted as marl deposited under open, clay rich conditions.

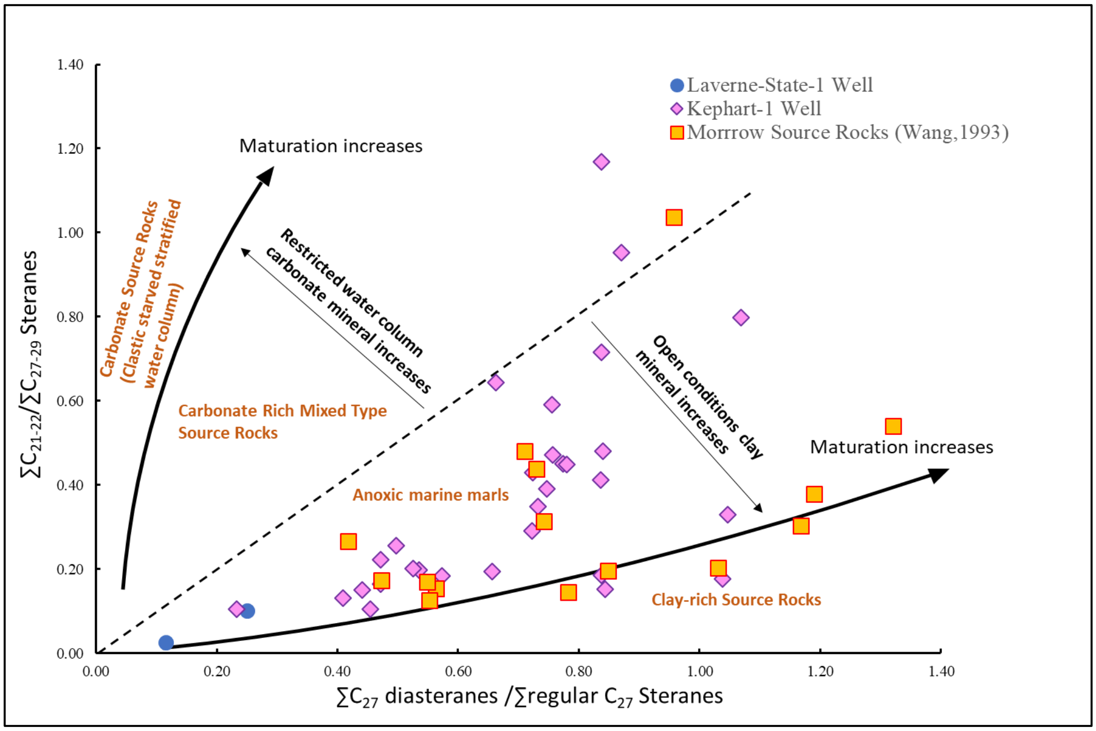


Figure 43. Plot of $\sum C_{21-22}/\sum C_{27-29}$ Steranes vs. $\sum C_{27}$ diasteranes /$\sum$regular C_{27} Steranes (Modified after Wang et al., 2015)

4.3.5.3 Diasteranes

Diasteranes or “rearranged steranes” are important for assessment of the lithology, redox conditions and the thermal maturity of source rocks (Kirk and Shaw, 1975; Moldowan et al. 1991a; Peters et al. 2005). Their structures differ from regular steranes in that they have a methyl group attached to C-5 and C-14 and hydrogens attached to C-10 and C-13 (Waples and Machihara, 1991). Rubinstein et al. (1975) proposed that the diasteranes are most readily present in clastic sediments, and the acidic clays in them play the essential role for the conversion of the diasteranes from the regular steranes. Therefore, they are useful for distinguishing carbonate source rocks from clastic source rocks (Wang et al., 2015). Moldowan et al. (1991b) noticed that the diasteranes are also abundant in the organic-lean Adriatic Basin carbonates deposited under low pH and high Eh conditions and therefore suggested that their presence may be also associated with redox conditions. In the following years, Moldowan et al. (1994) showed that there is a positive correlation between increasing Pr/(Pr+Ph) value and C_{27} diasteranes (**XXIV**) in Toarcian marine source rocks from southwest Germany. The authors proposed that oxicity and the clay content in the depositional environment are the two main factors controlling such a positive correlation in a way that oxic/suboxic shale strata tend to have higher C_{27} diasterane/(C_{27} diasteranes+C_{27} steranes) and Pr/(Pr+Ph) value than the anoxic carbonates. Besides their utility as a facies indicator, diasteranes are also useful to assess thermal maturity (Mackenzie et al., 1980). Diasteranes are more stable than regular steranes and therefore become more abundant with increasing maturity (Goodarzi et al., 1989) and biodegradation (Waples and Machihara, 1991). However, their utility as a maturity indicator should be used with caution since lithology has a big impact on the diasterane conversion (Waples and Machihara, 1991).

The Morrow source rocks, in general, are characterized with high concentrations of diasteranes although their relative concentration is generally lower than the regular steranes. The C_{27} diasteranes are the most dominant among the others and in a few samples their concentrations are even higher than the regular steranes such as in MOR-2, MOR-57, MOR-68 and MOR-74. The high diasterane values in those samples is either maturity related or related to high clay content and increasing oxic conditions in the depositional environment.

4.3.6. Polycyclic Aromatic Hydrocarbons

The polycyclic aromatic hydrocarbons (PAHs) of pyrolytic origin are the result of incomplete combustion of the organic matter present in the sediments and oils (Killops and Massoud, 1992; Brewster et al., 2017) while some of the PAHs are generated by the diagenetic and catagenetic alterations of the organic matter (Li et al., 2013). They are commonly found in high concentrations in the coals that derived from terrestrial higher plants (Tissot and Welte, 1984; Armstroff et al., 2006) and are widely found in the Late Paleozoic sediments and oils due to the significant diversification and expansion of land plants during this period (Armstroff et al., 2006). The main mechanisms that caused the generation of PAHs were paleo-fires commenced with lightning strikes (Chaloner, 1989), igneous (Murchison and Raymond, 1989) and hydrothermal activities (Kawka and Simoneit, 1990) that result in diagenetic and catagenetic alterations of the organic matter. Although the utility of PAHs in petroleum geochemistry is not as widespread as aliphatic compounds, they are widely accepted as maturity indicators, and can provide valuable information on the type of organic matter input, depositional environment, oil migration, paleo-wild fires, maturity or diagenesis of the organic matter (Sivan et al., 2008). However, the identification and the interpretation of the PAHs should be made with caution due to some uncertainties in their origin.

Since the identification of PAHs is difficult and they can be easily misidentified, a coal tar standard (Standard Reference Material 1597 National Bureau of Standards) was used for the identification of the dibenzothiophenes, dibenzofurans, benzofluoranthenes, pyrenes, benzopyrenes, cadalene, chrysene, benzoanthracene, and triphenylene compounds in the Morrow source rock samples whose significance will be discussed in the following parts.

4.3.6.1 PAHs as Depositional Environment and Source Indicator

4.3.6.1.1 Dibenzothiophene

Dibenzothiophene (DBT; **XXV**) is a sulfur-containing aromatic biomarker, which is highly resistant to biodegradation and increasing thermal maturity (Peters et al., 2005). It is widely associated with the H_2S rich anoxic conditions (Hughes et al., 1995) and when coupled with another aromatic biomarker, phenanthrene (P; **XXVI**), it provides valuable information about the depositional environment. For instance, Hughes et al. (1995) proposed a depositional environment classification scheme in which the ratios of dibenzothiophene/phenanthrene and pristane/phytane were plotted against each other. The scheme is mainly divided into the five different depositional environments based on the redox conditions and the reduced sulfur amount present within the depositional environment (Hughes et al., 1995). It provides a convenient and reliable approach to identify depositional environments and lithology of the source rocks since the ratios are resistant to biodegradation and thermal alterations (Hughes et al., 1995).

Dibenzothiophene and methyldibenzothiophenes (MDBT; **XXVII**) were identified in the Morrow source rock samples using m/z 184, m/z 198 and m/z 202 ion chromatograms as presented in the Figure 44. DBT and MDBT were detected in considerable amounts in the Morrow source rock samples with DBT being the most dominant and 1-MDBT being the least abundant dibenzothiophene homologue. Radke (1988) suggested that methyldibenzothiophenes were as useful as the methylphenanthrenes in terms of maturity assessment and added that 1-MDBT is thermally the least stable compound among other MDBTs. Radke (1988) added that the calculated vitrinite reflectance (Rc%) is showing a strong correlation, as indicated by the correlation coefficient (r= 0.84), with the mean vitrinite reflectance value (Rm%) for the source rocks at the oil window. The proposed methyldibenzothiophenes ratio (MDR) and the equation for the mean vitrinite reflectance value (Rm %) are as follows:

$$MDR = \frac{4-MDBT}{1-MDBT}$$

Radke (1988)

$$Rm\,\% = 0.51 + (0.073 * MDR)$$

Radke (1988)

The average MDR for the Wang (1993) source rock samples is 9.34 and the corresponding mean vitrinite reflectance, Rm%, value is 1.19 indicating that they are mainly in the late oil window. The average MDR of the Kephart-I Well is 4.05 and the corresponding Rm % value is 0.81 indicating that the Kephart-I is in the peak oil

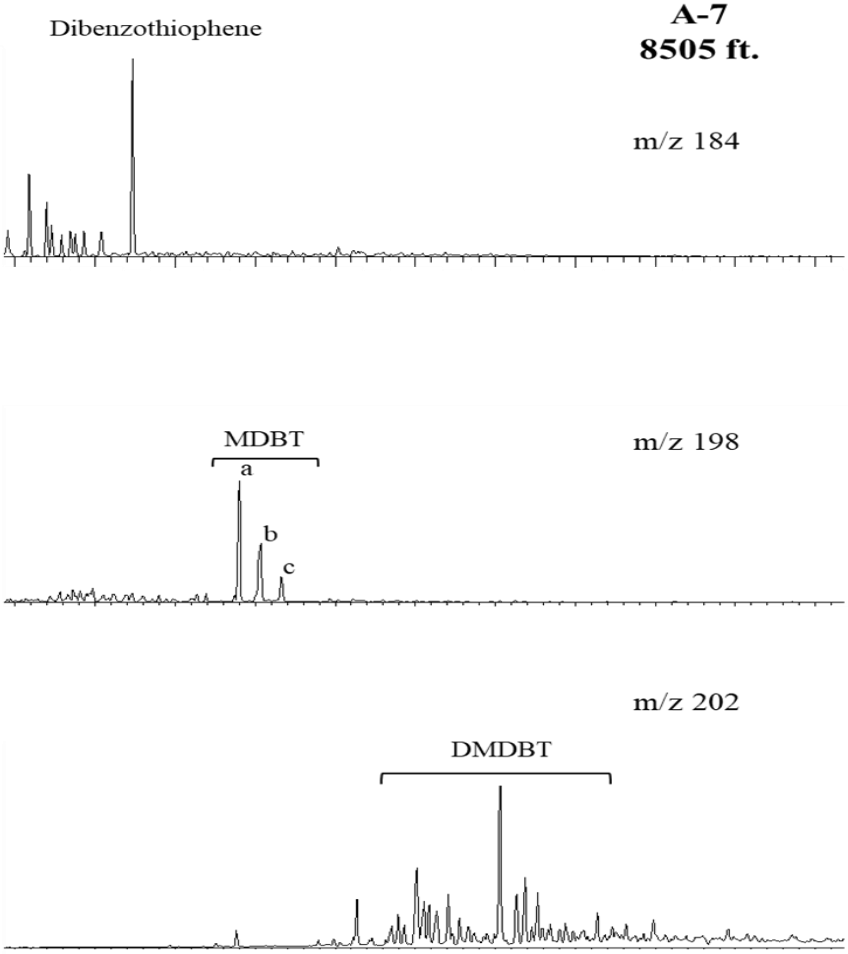


Figure 44. Identification of DBT, MDBT and DMDBT (a: 4-MDBT; b: 2-+3-MDBT; c: 1-MDBT)

generation window. Finally, the average MDR of the Laverne-State-I Well is 3.04 and the corresponding Rm % is 0.74 indicating that the samples are thermally mature and in the early oil window. The calculated MDR and Rm % values are given in the Table 12.

The cross plot of the DBT/P vs. Pr/Ph ratios of the Morrow source rock samples are dispersed in three zones. For instance, the Wang (1993) source rock samples and the majority of the Kephart-I Well samples fall into Zone 3 which is associated with either

Table 12. Calculated ratios of DBT/P, MPI-1, Rc%, log(1,2,5-TMN/1,3,6-TMN), log(1,2,7-TMN/1,3,7-TMN), BaA/(BaA+Chrysene), MDR, Rm%

SAMPLE ID	DBT/P	MPI-1	Rc %	log (1,2,5 TMN/ 1,3,6 TMN)	log (1,2,7 TMN/ 1,3,7 TMN)	1,2,8-TMP/ C_3 Phenanthrenes	BaA / (BaA + chrysene)	MDR	Rm %
A-1	0.2	1.2	1.1	-0.5	-0.5	0.5	0.2	4.7	0.9
A-2	0.1	1.4	1.27	-0.38	-0.34	0.45	0.03	6.12	0.96
A-3	0.2	1.1	1.1	-0.4	-0.4	0.9	0.0	3.0	0.7
A-4	0.2	1.3	1.18	-0.17	-0.11	0.48	0.07	6.99	1.02
A-5	0.2	1.3	1.2	-0.5	-0.5	0.5	0.4	3.4	0.8
A-6	0.3	1.3	1.20	-0.47	-0.47	0.51	0.15	3.93	0.80
A-7	0.3	1.3	1.2	-0.4	-0.3	0.5	0.2	4.1	0.8
A-8	0.2	1.3	1.15	-0.48	-0.49	0.54	0.10	4.54	0.84
A-9	0.2	1.3	1.2	-0.5	-0.5	0.6	0.2	4.4	0.8
A-10	0.3	1.3	1.17	-0.47	-0.45	0.67	0.07	4.16	0.81
A-11	0.2	1.2	1.1	-0.3	-0.4	0.5	0.1	3.4	0.8
A-12	0.2	1.4	1.24	-0.48	-0.39	0.56	0.11	2.30	0.68
A-13	0.2	1.4	1.2	-0.4	-0.3	0.6	0.1	4.8	0.9
A-14	0.1	1.4	1.23	-0.25	-0.20	0.54	0.14	2.97	0.73
A-15	0.1	1.4	1.2	-0.3	-0.3	0.4	0.2	7.2	1.0
A-16	0.1	1.4	1.22	-0.32	-0.24	0.44	0.16	2.69	0.71
A-17	1.7	1.5	1.3	-0.3	-0.2	0.4	0.2	3.0	0.7
A-18	0.1	1.4	1.26	-0.31	-0.35	0.41	0.19	2.71	0.71
A-19	0.2	1.5	1.3	-0.3	-0.4	0.5	0.2	2.6	0.7
A-20	0.1	1.5	1.28	-0.29	-0.23	0.44	0.15	3.21	0.74
A-21	0.1	1.5	1.3	-0.2	-0.2	0.4	0.2	3.3	0.7
A-22	0.1	1.5	1.29	-0.35	-0.37	0.43	0.21	3.93	0.80
A-23	0.1	1.5	1.3	-0.3	-0.2	0.4	0.2	4.6	0.8
A-24	0.1	1.5	1.32	-0.29	-0.22	0.36	0.25	4.38	0.83
A-25	0.1	1.4	1.3	-0.3	-0.3	0.4	0.2	6.6	1.0
A-26	0.1	1.4	1.22	-0.38	-0.42	0.47	0.17	6.81	1.01
A-27	0.1	1.4	1.2	-0.4	-0.4	0.6	0.2	3.0	0.7
A-28	0.1	1.3	1.20	-0.35	-0.30	0.55	0.17	2.70	0.71
A-29	0.4	1.5	1.3	-0.2	-0.3	0.4	0.1	3.3	0.8
A-30	0.1	1.1	1.05	-0.44	-0.48	0.88	0.05	2.69	0.71
H-2	0.1	1.1	1.1	-0.3	-0.5	0.5	0.3	3.0	0.7
H-3	0.1	1.3	1.20	-0.24	-0.16	1.11	0.35	3.10	0.74
MOR-2	0.1	0.9	0.9	-0.7	-0.6	0.0	0.0	11.5	1.4
MOR-11	0.1	1.0	0.99	-0.71	-0.59	0.01	0.08	16.71	1.73
MOR-16	0.1	3.1	2.3	-0.5	-0.4	0.0	0.0	11.6	1.4
MOR-33	0.0	0.6	0.78	-0.43	-0.39	0.06	0.03	1.96	0.65
MOR-39	0.4	1.1	1.1	-0.5	-0.4	0.0	0.0	15.5	1.6
MOR-41	0.0	1.6	1.37	-0.63	-0.49	0.02	0.06	9.51	1.20
MOR-43	0.1	1.0	1.0	-0.8	-0.6	0.0	0.0	18.6	1.9
MOR-57	0.1	0.8	0.85	-0.65	-0.48	0.05	0.29	7.69	1.07
MOR-66	0.0	0.6	0.8	-0.4	-0.3	0.1	0.0	3.4	0.8
MOR-64	0.1	0.7	0.85	-0.46	-0.35	0.10	0.02	4.92	0.87
MOR-68	0.0	0.9	0.9	-0.4	-0.4	0.1	0.0	6.8	1.0
MOR-74	0.0	1.7	1.45	-1.02	-0.78	0.01	0.05	13.42	1.49
MOR-75	0.1	0.6	0.8	-0.5	-0.4	0.1	0.5	5.2	0.9
MOR-86	0.0	0.8	0.91	-0.73	-0.67	0.03	0.07	6.00	0.95
MOR-91	0.1	1.3	1.2	-0.4	-0.3	0.1	0.1	7.3	1.0

marine or lacustrine shales (Figure 45). However, the upper parts of the Kephart-I well have lower Pr/Ph values that caused samples to fall into Zone 2 in the cross plot. Zone-2 indicates a sulfate-poor lacustrine depositional environment and for the Morrow source rocks it can also possibly be interpreted as increasing carbonate content and reducing conditions in the depositional environment. The Laverne-State-I samples show different origins as the H-3 sample fall into Zone 4 which is associated with the carbonaceous shale or coal deposited under fluvio-deltaic depositional environment, while the H-2 sample falls into Zone-3 as the majority of the Morrow source rocks (Figure 45).

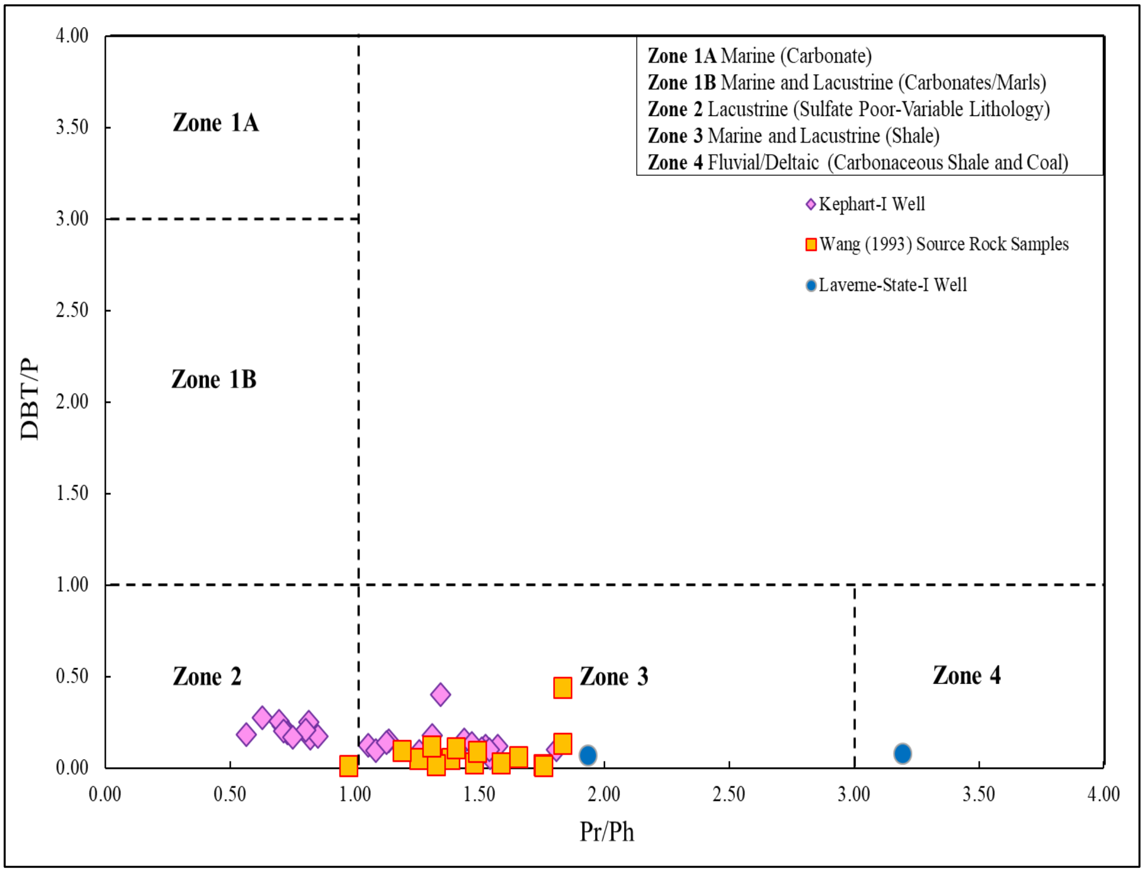


Figure 45. Cross plot of the DBT/P vs. Pr/Ph providing a novel and convenient way to identify source rock depositional environments and lithologies (Modified after Hughes et al., 1995).

4.3.6.1.2 Alkylnaphthalenes

High concentrations of alkylnaphthalenes (**XXVIII**) are observed in the Morrow source rock samples and a representative distribution of the alkyl naphthalenes is given in Figure 46 while Table 13 shows the compound identifications.

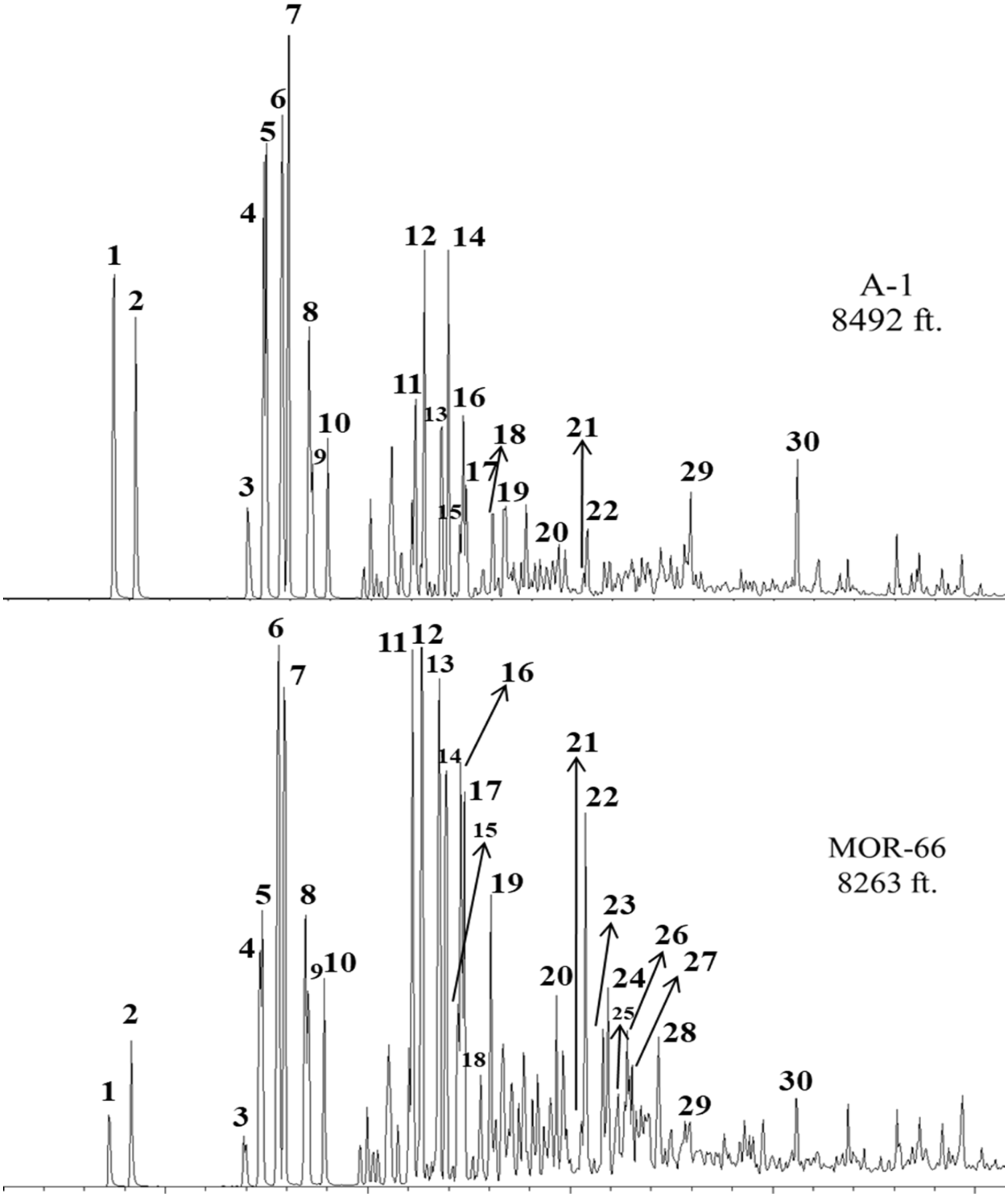


Figure 46. Mass chromatograms **(**m/z 142+156+170+184+198+212) of the naphthalene compounds in the Morrow Shale

Table 13. Naphthalene compound identification **(**m/z 142+156+170+184+198+212)

Peak No	**Compound**	**Peak No**	**Compound**
1	2-MN	**16**	1,6,7-TMN
2	1-MN	**17**	1,2,6-TMN
3	2-EN	**18**	1,2,4-TMN
4	2,6-DMN	**19**	1,2,5-TMN
5	2,7-DMN	**20**	1,3,5,7-TeMN
6	1,7-DMN	**21**	1,3,6,7-TeMN
7	1,3+1,6-DMN	**22**	Cadalene
8	1,4-DMN	**23**	1,4,6,7+1,2,4,6+1,2,4,7-TeMN
9	2,3-DMN	**24**	1,2,5,7-TeMN
10	1,2-DMN	**25**	2,3,6,7-TeMN
11	1,3,7-TMN	**26**	1,2,6,7-TeMN
12	1,3,6-TMN	**27**	1,2,3,7-TeMN
13	1,4,6+1,3,5TMN	**28**	1,2,5,6+1,2,3,5-TeMN
14	2,3,6-TMN	**29**	DBT
15	1,2,7-TMN	**30**	4MDBT+1,2,3,6,7-PMN

Alkylnaphthalenes mainly originate from the cyclic triterpenoids that are derived from the resins of the conifers and are closely related to terrestrial sources (Armstroff et al., 2006; Sivan et al., 2008). For instance, Strachan et al. (1988) observed significant amounts of 1,2,5-trimethylnaphthalene (1,2,5-TMN;**XXIX**) and 1,2,7-trimethylnaphthalene (1,2,7-TMN;**XXX**) in the samples having a Type-III kerogen and therefore proposed that the higher plants are the most likely precursor of 1,2,5-TMN and 1,2,7-TMN. Armstroff et al. (2006) suggested that 1,2,7-TMN was directly derived from oleanane-type triterpenoids present in angiosperms while 1,2,5-TMN could be produced from the non-angiosperm plants or dehydrogenation of agathic acid, communic acid and manool (Figure 47; Püttmann and Villar, 1987; Strachan et al., 1988). Both Strachan et al. (1988) and Armstroff et al. (2006) confirmed the presence of 1,2,5-TMN and 1,2,7-TMN in the pre-Cretaceous samples, however neither of them identified any oleanane in the samples which 1,2,5-TMN and 1,2,7-TMN were identified. Therefore, Armstroff et al. (2006) suggested that using 1,2,7-TMN as an angiosperm indicator is questionable since it may originate from another yet unknown natural source. However, the presence of oleanane in pre-Cretaceous samples described by Moldowan et al. (1994), Peters et al. (1999) and in the unpublished MS thesis of Wood (2017) supports the concept that 1,2,7-TMN and 18α(H)-oleanane are viable biomarkers associated with the angiosperms. This study also confirms that 1,2,7-TMN is found in significant concentrations in all of the Morrow source rock samples that were analyzed. Their occurrence in the Morrow samples is supporting evidence for 18α(H)-oleanane and 1,2,7-TMN being related.

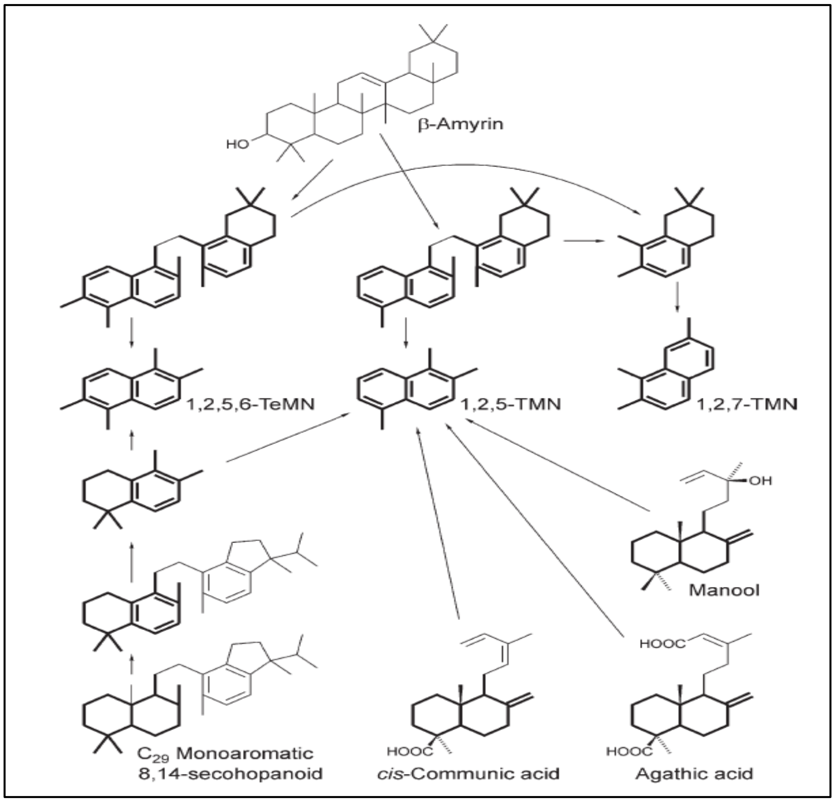


Figure 47. Possible biological precursors and pathways for the generation of 1,2,5-trimethylnaphthalene (1,2,5-TMN) and 1,2,7-trimethylnaphthalene (1,2,7-TMN; Armstroff et al., 2006)

The presence of 1,2,7-TMN in the Morrow source rock samples was unexpected, as was the tentative presence of oleanane, since it is widely accepted that this compound is related to 18α(H)–oleanane which is an age specific biomarker used for Cretaceous and younger source rocks and oils (Armstroff et al., 2006). 1,2,7-TMN was identified in all the Morrow samples and in a few of them oleanane was absent or in trace amounts (Figure 48; Table 9). The reason for this contradiction can be related to depositional conditions of the Morrow Shale as discussed previously. Increasing freshwater conditions during the deposition of the Morrow could prompt the degradation and aromatization of the oleanane and therefore no oleanane could possibly be preserved in those samples. Alternatively, 1,2,7-TMN may not be affected by the salinity of the environment and thus high concentrations of 1,2,7-TMN could be preserved in the depositional environment (McCaffrey et al., 1994; Murray et al., 1997a; Al-Ameri et al., 2010). Another possibility is that the presence of seawater in the depositional environment which could help the preservation of the oleanane by improving hydrogenation (McCaffrey et al., 1994; Murray et al., 1997a). Murray et al. (1997a) suggested that 18α(H)–oleanane is highly susceptible to depositional conditions and the diagenetic alteration of the β-amyrin in terrestrial environments are dominated by the aromatic pathway which results in generation of a higher concentrations of aromatic oleanoid compounds instead of saturated oleanane type compounds. For instance, 18α(H)–oleanane deposited under a marine influenced deltaic environment, as in the Morrow source rock, could possibly be preserved better than the 18α(H)–oleanane deposited under more terrestrial conditions (Murray et al., 1997a). It is because of the fact that, in terrestrial environments with high sediment influx, preservation of β-amyrin as a saturated oleanane derivative is unlikely when compared to aromatization of β-amyrin and occurrence as an aromatic oleanoid compound. Thus, the presence of 18α(H)–oleanane and 1,2,7-TMN in the Morrow source rocks supports the concept that these compounds are probably related and are still reliable biomarkers to infer the presence of angiosperms.

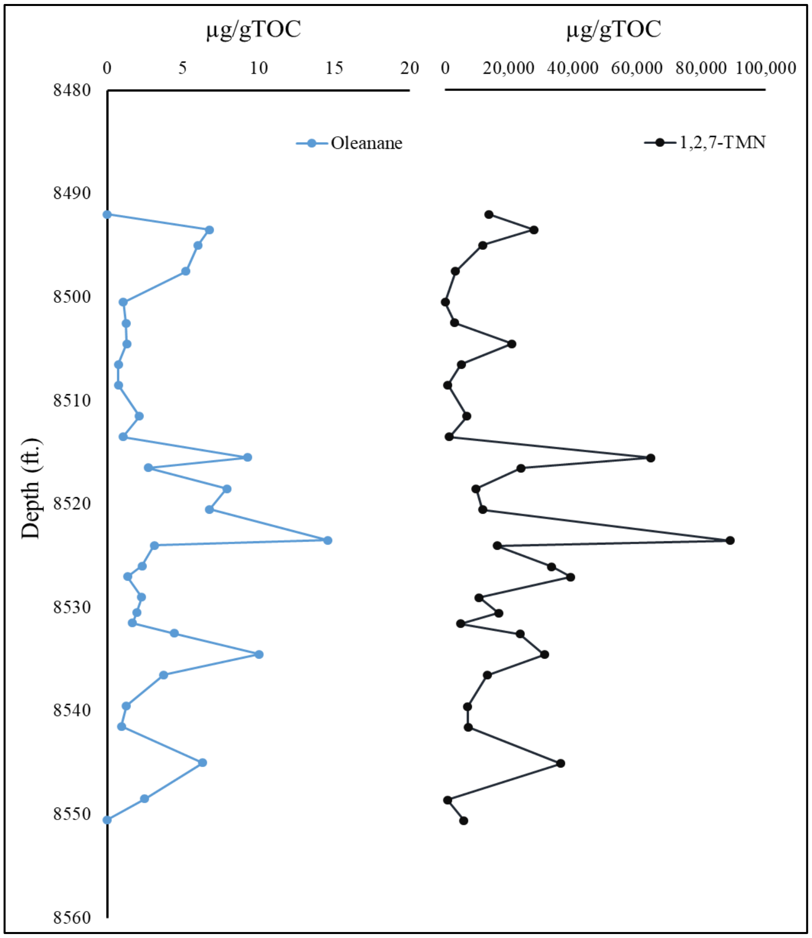


Figure 48. 18α(H)–Oleanane and 1,2,7-TMN concentrations found in the Kephart-I well.

A logarithmic plot of the ratio 1,2,5-TMN/1,3,6-TMN against the ratio 1,2,7-TMN/1,3,7-TMN for the Morrow source rock samples is given in the Figure 49. The plot was originally proposed by Strachan et al. (1988) in order to assess the TMN contributions of different depositional environments. The plot proposed by Strachan et al. (1988) when applied to the samples analyzed in this study reveals that 1,2,7-TMN and 1,2,5-TMN are found in considerable amounts in most of the studied samples. However, few of the Wang (1993) Morrow source rock samples fall in to the lower left quadrant of the plot. Although these samples have close log(1,2,5-TMN/1,3,6-TMN) and log(1,2,7-TMN/1,3,7-TMN) values; 1,2,5-TMN and 1,2,7- TMN was comparatively lower than the

1.3,7- TMN and 1,3,6-TMN concentration. Armstroff et al. (2006) mentioned that 1,2,5 TMN is derived from gymnosperms and its strong correlation with 1,7-dimethylphenanthrene indicates that its potential precursor is agathic acid. Therefore, lower concentrations of 1,2,5-TMN and 1,2,7- TMN indicate either lesser amounts of higher plant input or the higher plant input was sufficient but the aromatization process did not prevail. However, it should be noted that the samples that fall into the lower left quadrant are the ones that are deposited very close to the deeper Anadarko Basin and thus buried at the depths more than or very close to 10,000 ft. and they have relatively higher maturities with significant aromatic concentrations. Therefore, the most probable reason for the lower amounts of 1,2,5-TMN and 1,2,7-TMN, and higher concentrations of 1.3,7-TMN and 1,3,6-TMN is the low amount of terrestrial input to the depositional environment.

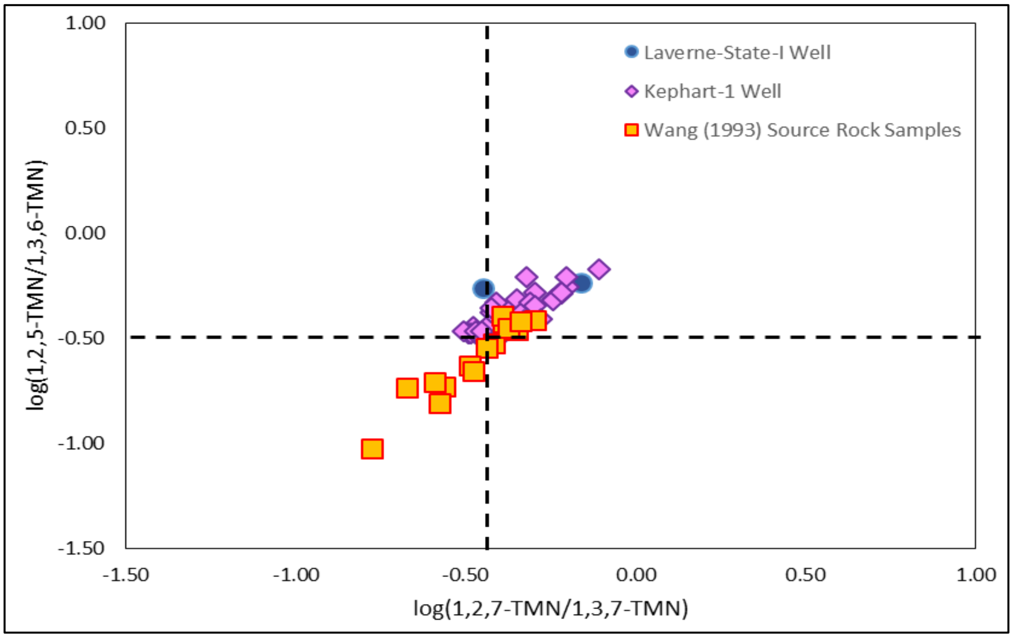


Figure 49. Cross plot of the logarithm of the 1,2,7-TMN/1,3,7-TMN ratio vs. the logarithm of the 1,2,5- TMN/1,3,6-TMN ratio (Modified after Strachan et al. (1988) (The solid lines represent benchmark values for the two ratios, derived from values found in the most mature sample from the Kephart-I Well)

4.3.6.1.3 Cadalene, Fluorene, Dibenzofuran and Its Alkyl Derivatives

Another PAH compound identified in the Morrow source rock is cadalene (**XXXI**) which is an aromatic bicyclic sesquiterpenoid that appears in the m/z 184 ion chromatogram. Since cadalene was not present in the coal tar standard, it was identified by comparison with the retention time from the co-injection of a cadalene standard in a prior GC-MS analysis (Jones, 2017; Figure 50). Although cadalene has been widely used as a higher plant indicator due to its ubiquity in many higher plants, Elias et al. (1997) proposed that they can be also derived from the algal biomasses found in a lagoonal environment. Therefore, cadalene may not be as reliable as 1,2,7-TMN or 1,2,5-TMN for the assessment of higher plant input (van Aarssen et al., 2000). Nevertheless, identifying cadalene in most of the Morrow source rock samples in high concentration supports the evidence discussed earlier that indicating periodic higher plant input during deposition.

Fluorene (Fl; **XXXII**), dibenzofuran (DBF; **XXXIII**) and its methylated derivatives (MDBF; **XXXIV**) are other PAHs identified in the Morrow source rock samples (m/z 166, m/z 168 and m/z 182, respectively; Figure 51). Li et al. (2013) observed that fluvial/deltaic/freshwater lacustrine shales are dominated by fluorene while dibenzofuran abundant in coal samples deposited in a swamp environment (Pu et al., 1990; Li et al., 2004). Moreover, Radke et al. (2000) proposed that MDBF are potential biomarkers of lichens that have symbiotic relationship between a fungus and a green algae. Overall, the presence of terrestrial indicative PAHs such as fluorene, dibenzofuran and methylated derivatives are indicative of terrestrial freshwater conditions that prevailed during the deposition of the Morrow source rocks. While the samples with high Fl, DBF and its MDBF concentrations might belong to more proximal parts of the basin, the samples with low Fl, DBF and its MDBF concentration were probably deposited in more distal parts of the basin (i.e prodelta).

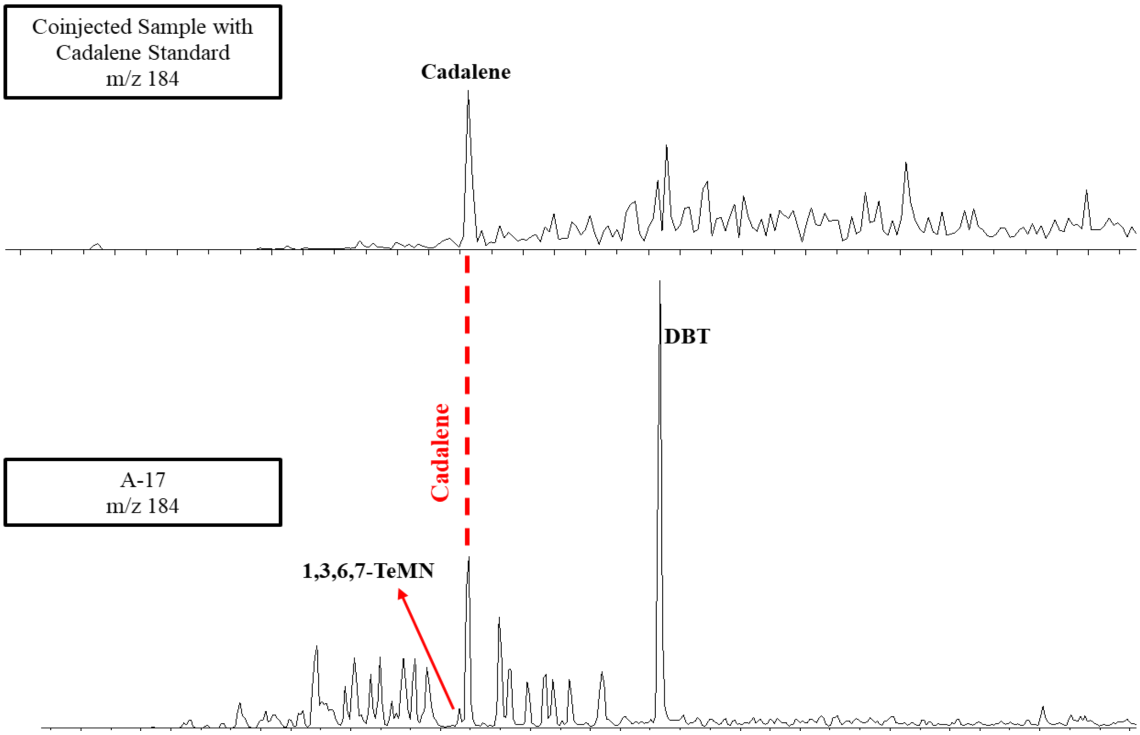


Figure 50. m/z 184 ion chromatogram of the A-17 sample**.** Cadalene was identified by comparison with retention time in the co-injection of cadalene internal standard

4.3.6.1.4 Alkylphenanthrenes as Maturity and Potential Source Indicators

The main, and widely accepted, use of the alkylphenanthrenes is as a maturity parameter (Radke et al., 1982; Peters et al., 2005; Armstroff et al., 2006). Radke et al. (1982) observed that 9-methylphenanthrene (9-MP) and 1-methylphenanthrene (1-MP) are highly abundant in the immature source rocks with 9-MP typically more dominant than 1-MP. Moreover, with the increasing maturity, 9-MP and 1-MP lose their predominance and 2-methylphenanthrene (2-MP) and 3-methylphenanthrene (3-MP) increase in relative concentration with 2-MP being predominant (Radke et al., 1982). Based on these observations, Radke et al. (1982) proposed a convenient and reliable

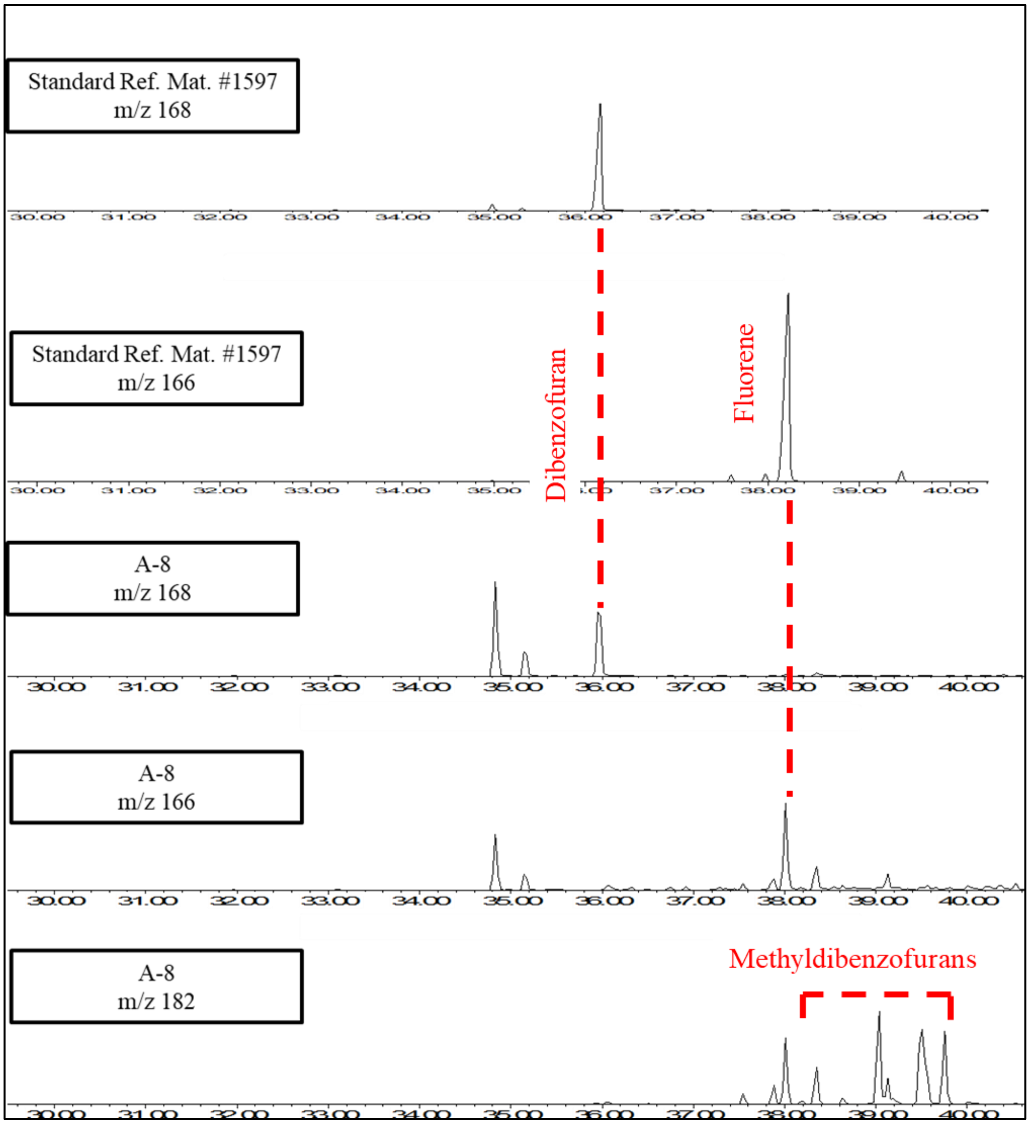


Figure 51. GCMS identification of dibenzofuran, fluorene and methyldibenzofuran confirmed by comparison with coal tar standard

approach, namely the Methylphenanthrene Index (MPI), to assess the thermal maturity of coals and Type-III kerogens. The approach was subsequently extended to Type-I and Type-II kerogens and oils. The authors suggested that the MPI reduces the effects of facies variations in thermal maturity so that it provides an accurate maturity measurement (Radke et al., 1982 and 1986). The MPI showed good correlation with the vitrinite reflectance of shale and coals containing Type III organic matter (Radke and Welte, 1983;

Armstroff et al., 2006). The calibration between vitrinite reflectance and MPI is given in the Figure 52 (Peters et al., 2005). The relationship between MPI-1 and R_c is as follows:

$$\boldsymbol{MPI\ 1} = 1.5 * \frac{(2MP + 3MP)}{(P + 1MP + 9MP)}$$

$$\boldsymbol{R_C} = 0.6 * MPI\ 1 + 0.4\ for\ R_0 < 1.35\ \%$$

$$\boldsymbol{R_C} = -0.6 * MPI\ 1 + 2.3\ for\ R_0 > 1.35\ \%$$

Radke et al. (1982) proposed positive and negative correlation lines based on the maturity level of the samples. Positive correlation line can be used for the samples in the oil window (0.65< R_0% <1.35) while negative correlation line can be used for the samples with high maturity (1.35 <R_0% < 2.00). In this study, positive linear correlation line was used for calibration between MPI-1 and R_0 %.

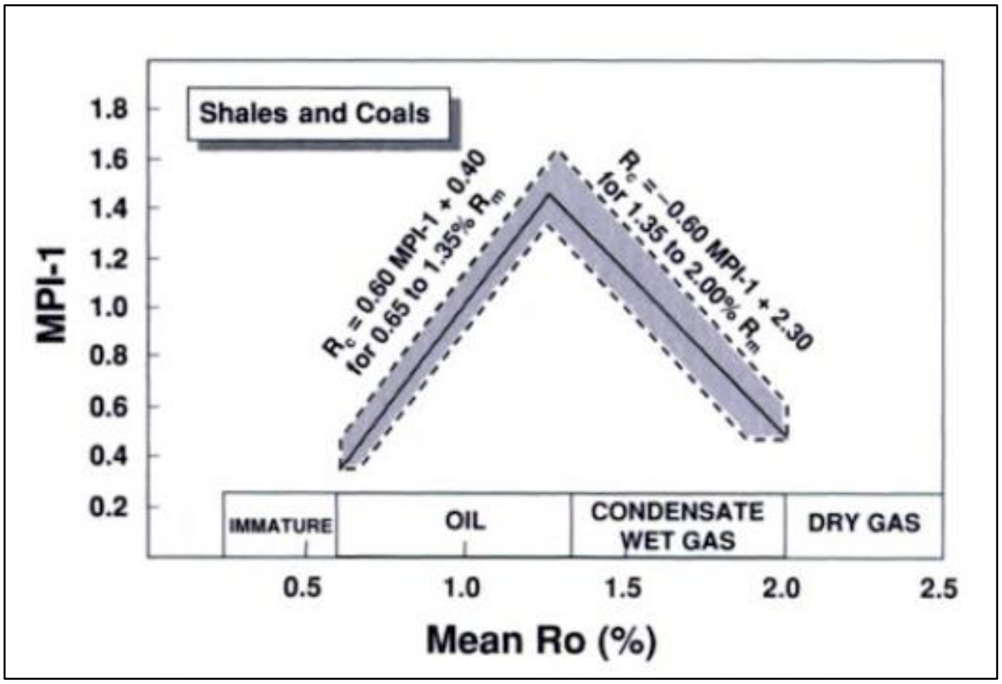


Figure 52. The calibration between MPI-1 and vitrinite reflectance is based on shales and coals containing Type-III organic matter (Radke and Welte, 1983; Peters et al., 2005)

The distribution of the alkylphenanthrenes in the Morrow Formation are illustrated in Figure 53 and compound identifications are given in Table 14. The alkylphenanthrenes of 9-MP, 1-MP, 3-MP and 2-MP were used to calculate MPI-1 ratios (Table 12). For instance, the average MPI-1 value of the Wang (1993) source rock samples is 1.13 and ranges from 0.61 to 3.14. The corresponding calculated vitrinite reflectance values range between 0.77% and 2.28% with an average of 1.08%. The average MPI-1 values of the Kephart-I well is 1.36 and ranges between 1.09 and 1.53. The average calculated vitrinite reflectance value for the Kephart-I Well is 1.22% and ranges between 1.05% and 1.28%. Finally, the average MPI-1 value of the Laverne-State-I Well samples is 1.23 and average calculated vitrine reflectance value is 1.14%. In general, MPI-1 value of the Morrow source rock samples indicate that they are thermally mature, and at or above the peak oil generation zone. The results are also parallel with the thermal maturity results obtained by MDR and Rm % values that were discussed previously.

Alkylphenanthrenes have been widely used as maturity indicators but their utility as source indicators are somewhat limited (Armstroff et al., 2006). Budzinski et al. (1993) observed relatively high amounts of 1,2,8-trimethylphenanthrene (1,2,8-TMP; **XXXV**) in coals and crude oils from Mahakam Delta and suggested that its occurrence was related with the degradation of the β-amyrin. Budzinski et al. (1995) also identified significant amounts of 1,2,8-TMP in marine oils and concluded that their ubiquitous occurrence indicates that they might have originated from the degradation of triterpenoids or hopanoids and not specifically β-amyrin. The studies of Garrigues et al. (1987) and

Killops (1991) also concluded that 1,2,8-TMP is possibly derived from the degradation of hopanoids. Revill et al. (1993) found significant amount of 1,2,8-TMP in *Tasmanites*

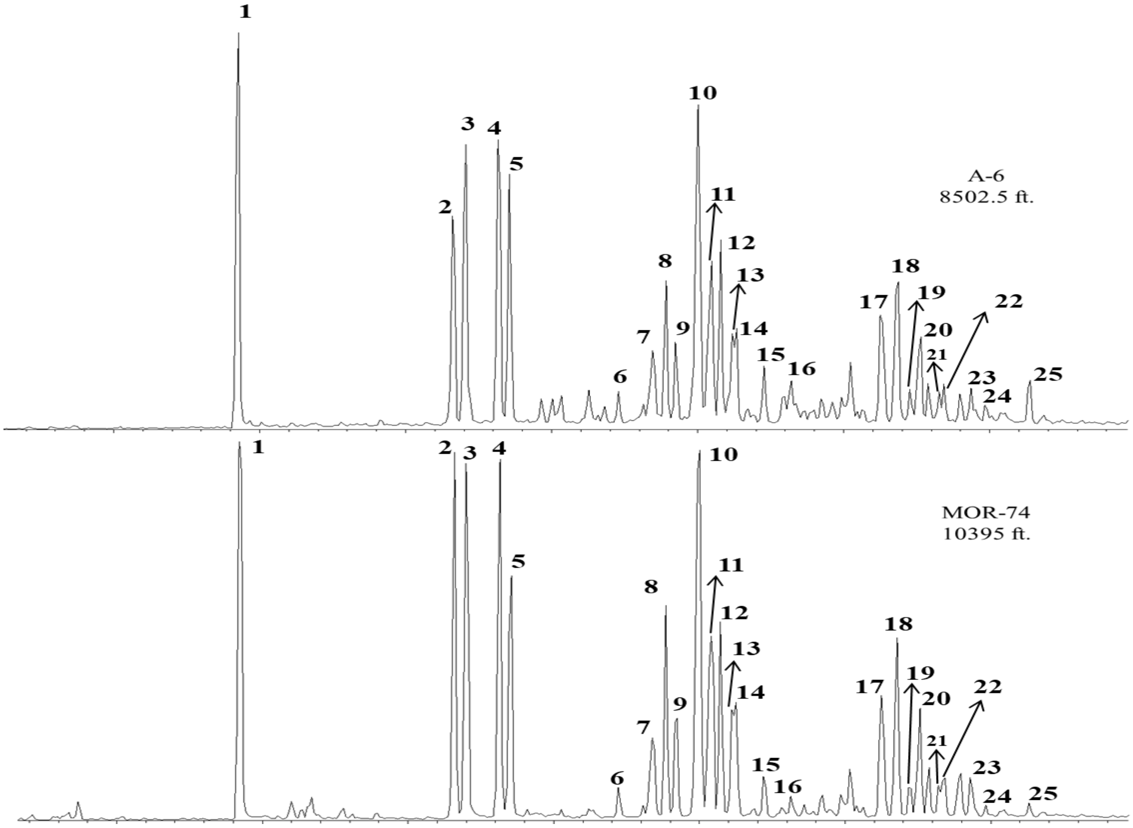


Figure 53. Mass chromatogram of the phenanthrene compounds of the Morrow Shale (m/z 178+192+206+220)

Table 14. Phenanthrene compound identification (m/z 178+192+206+220)

Peak No	Compound	Peak No	Compound
1	P	14	1,9-+4,9-+4,10-DMP
2	3-MP	15	1,8-DMP
3	2-MP	16	1,2-DMP
4	9-MP	17	1,3,6+1,3,10+2,6,10-TMP
5	1-MP	18	1,3,7-+2,6,9+2,7,9-+7-E-1-MP
6	3-EP	19	1,3,9-+2,3,6-TMP
7	9-,2-,1-EP+3,6-DMP	20	1,6,9-+1,7,9-+2,3,7-TMP
8	3,5-+2,6-DMP	21	1,3,8-TMP
9	2,7-DMP	22	2,3,10-TMP
10	1,3-+2,10-+3,9-+3,10-DMP	23	1,6,7-TMP
11	2,5-+2,9-+1,6-DMP	24	1,2,6-TMP
12	1,7-DMP	25	1,2,8-TMP
13	2,3-DMP		

oil shales and concluded that its occurrence is not specific for a certain depositional environment and they can be related to a bacterial, algal or terrestrial origin. Budzinski et al. (1993) and Armstroff et al. (2006) mentioned that the presence of 1,2,8-TMP is also highly affected by the thermal maturity.

1,2,8-TMP has been identified in all of the Morrow source rock samples in this study. Budzinski et al. (1995) suggested that a high proportion of 1,2,8-TMP may indicate low maturity and such a relation has been also observed in the Morrow samples that are in the early-oil window . For instance, MOR-16 which is one of the most mature samples within the data set has 1,2,8-TMP/$\sum C_3$ –Phenanthrenes (C_3(P)) ratio of 0.02 while MOR-64, MOR-66 and MOR-68, the least mature samples in the data set, have 1,2,8-TMP/C_3(P) ratio of 0.1, 0.11 and 0.1, respectively. The relative abundance of 1,2,8-TMP to C_3(P) is significantly higher in the Kephart-I and Laverne-State-I core samples compared to the Wang (1993) source rock samples. This might be related to facies variations (Armstroff et al., 2006) or maturity (Budzinski et al., 1995). For instance, Armstroff et al. (2006) pointed out that facies variations plays an important role in the varying proportions of 1,2,8-TMP. Wang's (1993) samples are widely distributed in the Anadarko Basin and therefore they might be composed of different facies assemblages compared to the Kephart-I and Laverne-State-I Well samples leading to differences in the 1,2,8-TMP/ C_3(P) ratio. Alternatively, Wang's (1993) samples are more mature than the Kephart-I and Laverne-State-I Wells and this is another possible explanation for the different concentrations of 1,2,8-TMP in the different data sets as the relative concentration of 1,2,8-TMP was proposed to be highly dependent on maturity. Lastly, Wang's (1993) fractionation method (thin layer chromatography) could be possibly not as effective as the fractionation method used in this study (column chromatography) which might result in less recovery of aromatic compounds and lower concentration of 1,2,8-TMP compared to this study.

4.3.6.2 PAHs as Paleo-wildfire Indicators

Wildfires natural disasters primarily initiated by lightning strikes (Scott, 2000), have been a part of the terrestrial ecosystem since the first land plants started to develop (dos Santos et al., 2016). Forest fires can be traceable in Earth's history by use of fossil charcoals and pyrogenic PAHs. For instance, the first paleo-wildfire was recorded by use of fossil charcoals in the Silurian (Glasspool et al., 2004) while pyrolytic PAHs help tracing back the paleo-fires from at least the Late Devonian (Scott, 1989).

In this study, pyrolytic PAH biomarkers such as pyrene (**XXXVI**), fluoranthene (**XXXVII**), benzopyrenes (**XXXVIIIa, XXXVIIIb**), benzofluoranthenes (**XXXIXa, XXXIXb, XXXIXc**), benzo(a)anthracene (BaA; **XL**), triphenylene(TPn; **XLI**) and chrysene (**XLII**) were detected in considerable amounts indicating paleo-wildfires during deposition of the Morrow. Interestingly, perylene was not detected in the Morrow source rock samples. The origin of perylene has been debated for a long time. While some papers suggest perylene can originate from both marine and terrestrial origin, in a detailed review of published data Marynowski et al. (2015) pointed out that perylene is preferentially associated with terrestrial organic matter. Furthermore, Louda and Baker (1984), Jiang et al. (2000), and Marynowski et al. (2015) suggested a genetic relationship between wood-degrading fungi and perylene. Nevertheless, Marynowski et al. (2015) added that the use of perylene as a wood-degrading fungi tracer is limited to the samples that are immature or below the peak oil generation. This possibly explains the scarcity of the perylene in the Morrow source rock samples as they are mostly at or above the peak oil generation zone (Marynowski et al., 2015).

Benzo(a)anthracene, chrysene and triphenylene were identified using the m/z 228 ion chromatogram from the GC-MS analysis and comparison with the coal tar standard (Standard Reference Material 1597; Figure 54).

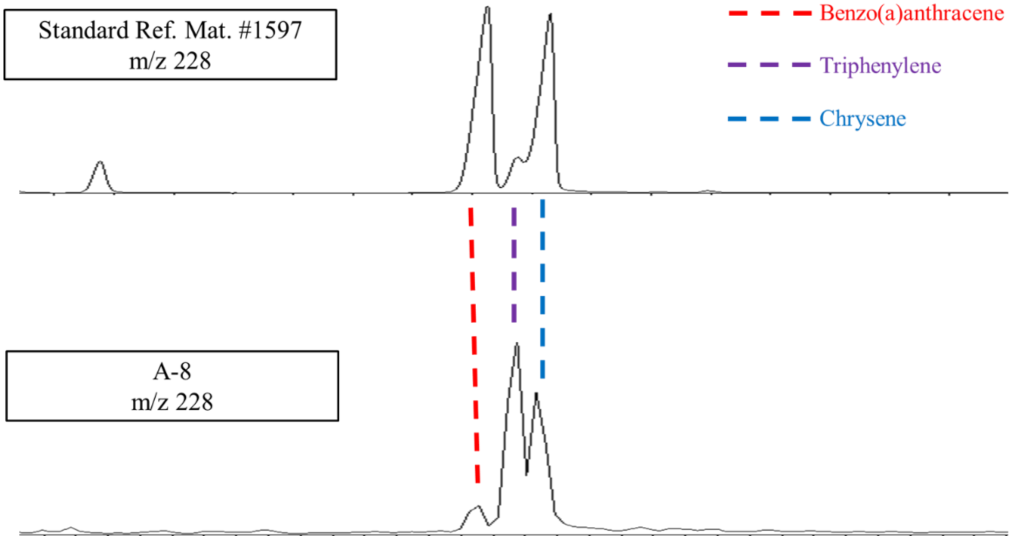


Figure 54. Identification of the benzoanthracene, chrysene and triphenylene with comparison to the coal tar standard

Chrysene and triphenylene can be produced by sedimentary diagenesis of the terpenoids (Tan et al., 1996) and/or partial combustion of terrestrial organic matter (Killops and Massoud, 1992; Jiang et al., 1998) while benzo(a)anthracene (BaA) can be only produced by the partial combustion of the organic matter (Laflamme and Hites, 1979). Yunker et al. (2002) proposed for recent sediments that chrysene is derived from partial combustion of terrestrial plants if the ratio of BaA / (BaA + chrysene) is less than 0.2 and derived by diagenetic alteration of the organic matter if the ratio is greater than 0.35. Values between 0.2 and 0.35 indicate either diagenetic or combustion inputs. Based on this suggestion, chrysene in the Morrow samples is mainly derived from the partial combustion of terrestrial organic matter as the average BaA / (BaA + chrysene) ratio for the Wang (1993) source rock samples is 0.09 while this value is 0.15 for the Kephart-I Well (Table 12). On the other hand, the average BaA / (BaA + chrysene) ratio of the Laverne-State-I Well is 0.34, which indicates that chrysene might be derived from the diagenetic alteration of terrestrial organic matter in the area of that core.

Finally, pyrene, fluoranthene, benzopyrenes and benzofluoranthenes were identified from the m/z 202 and m/z 252 ion chromatograms and comparison with the coal tar standard (Standard Reference Material 1597; Figure 55). These compounds are proposed to be produced from combustion of organic matter (Laflamme and Hites, 1979; Jiang et al., 1998).

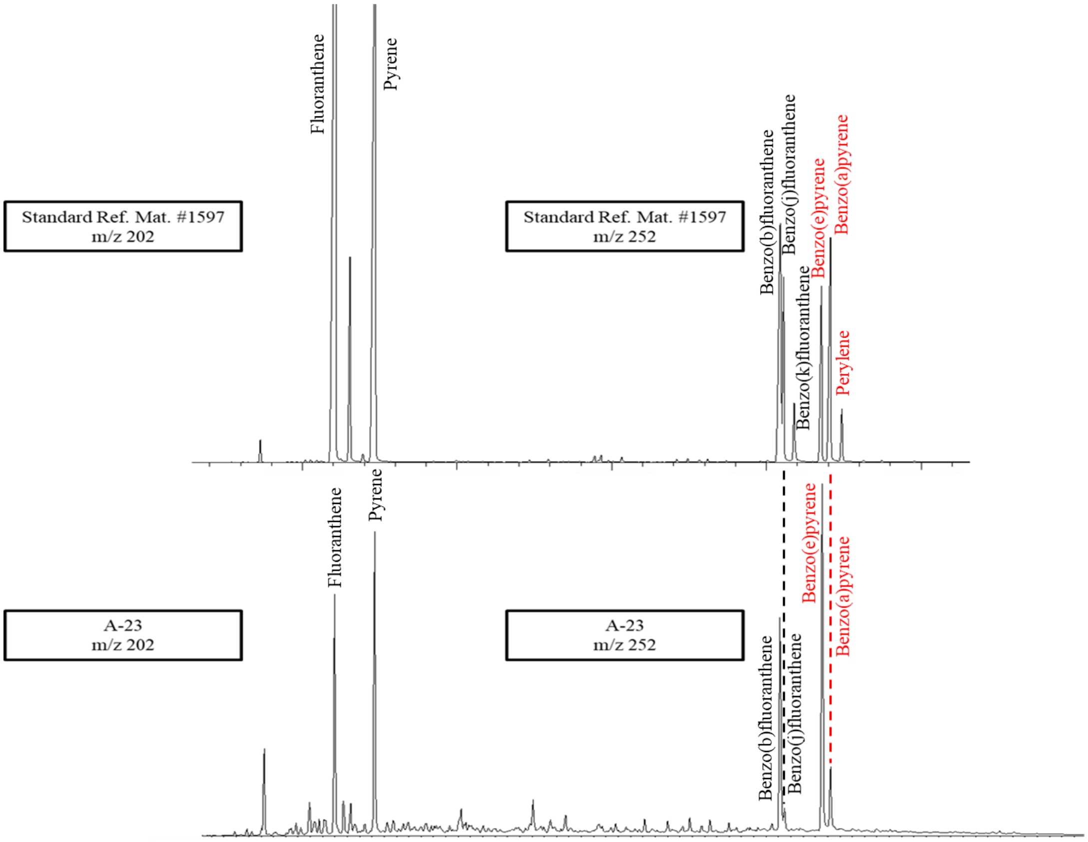


Figure 55. Identification of pyrene, fluoranthene, benzopyrenes and benzofluoranthenes using m/z 202+252 chromatogram

Chapter 5: Conclusions

Rock-Eval Pyrolysis and Leco TOC results indicate that the Morrow Shale is a good quality source rock characterized with Type-III kerogen derived from woody terrestrial plants. The n-alkane and sterane distributions of the Morrow show that it is composed of mixed type of organic matter that is derived from marine plankton and higher plants. The Morrow Shale was deposited under highly dynamic conditions and does not fit into a simple depositional model. Nevertheless, the biomarker analysis indicated that the Morrow Shale was deposited at a near-shore/transitional depositional environment which was subjected to periodic terrigenous influx by the fluvio-deltaic regimes. Some localized areas in the basin show a stratigraphic transition in depositional environment from marine to subaerial depositional conditions such as fluvial channels or marshes. Frequent sea-level changes during the Early Pennsylvanian time caused sub-oxic depositional conditions for the Morrow was supported with the isoprenoid ratios (Pr/Ph) between 1 and 3. The absence of gammacerane and C_{26}/C_{25} tricyclic terpane ratio were interpreted as low salinity brackish/freshwater conditions for the Morrow. The calculated vitrinite reflectance values and biomarker parameters revealed that the organic matter in the Morrow is thermally mature ranging between the early oil-window and the wet-condensate zone depending on the burial depth in the Anadarko Basin.

18α(H)-Oleanane has been tentatively identified in most of the Morrow source rock samples. The presence of 18α(H)-oleanane in pre-Cretaceous source rock samples is unusual and indicates that either 18α(H)-oleanane is derived from the earliest angiosperms which evolved long before the Cretaceous (Ramshaw et al., 1972; Martin et al., 1989) or originated from the non-angiosperm seed plants that share significant common characteristics with the angiosperms and are capable of synthesizing β-amyrin or other related compounds that are capable of producing 18α(H)-oleanane (Taylor et al., 2006).

Demethylated hopanes (such as 25-norhopane, 25,28,30-trisnorhopane, 25,30-bisnorhopane) were identified in multiple source rock samples. Since they are commonly associated with heavily biodegraded oils and are not found as the thermal degradation products of the kerogen, their presence in the Morrow source rocks was possibly related to organic matter re-working. They could possibly re-enter the sedimentary environment of the Morrow from an already biodegraded oil derived from an ancient reservoir (Noble et al., 1985). Another possible mechanism is the *in-situ* biodegradation of the oil, which had seeped from an ancient reservoir and was trapped in the fissures of the Morrow source rock (Noble et al., 1985). Finally, and least likely, their presence can be related to a specific type of microorganism, which is very uncommon, capable of producing demethylated hopanes (Peters et al., 2005).

1,2,7-TMN and 1,2,5-TMN are found in relatively high concentrations in most of the samples studied. The presence of 1,2,7-TMN in the Morrow source rocks and the pre-Cretaceous samples characterized by Moldowan et al. (1994), Peters et al. (1999) and unpublished MS Thesis of Wood (2017) supports the concept that the 1,2,7-TMN and 18α(H)-oleanane are viable biomarkers associated with the angiosperms and they are possibly derived from the earliest form of the angiosperms as suggested above. Although unlikely, it is still possible that there is another precursor of the 1,2,7-TMN which has not yet been discovered.

Finally the presence of evidence for paleo-wildfires was traced back to the Early Pennsylvanian time with presence of pyrolytic PAHs such as pyrene, fluoranthene, benzopyrenes, benzofluoranthenes, benzo(a)anthracene, triphenylene, and chrysene in the Morrow source rock samples. The PAHs with diagenetic origins (such as cadalene, fluorene and dibenzofuran) provided supporting evidence for the terrestrial organic matter deposited at fluvio-deltaic freshwater shales.

In summary, this comprehensive geochemical analysis on the Morrow Shale will help to fill the gap in the literature on geochemical characteristics of the Morrow Formation and might lead to new attempts for unconventional exploration and production in the Morrow. Morrow source rocks are fair to good source rocks, characterized by Type-III kerogen that has gas generating capacity and is thermally mature. It shows both terrestrial and marine character with terrestrial being the more dominant. Both the bulk geochemical and biomarker data indicate that the Morrow has heterogeneous facies characteristic in the Anadarko Basin since it was deposited under dynamic depositional conditions. The maturity analyses demonstrate that the maturity of the Morrow varies significantly in the Anadarko Basin depending on the burial depth. Additionally, pentacyclic terpane distributions revealed that the Morrow Shale possibly received a hydrocarbon charge from an ancient reservoir in the Anadarko Basin.

Overall, this study will make a good contribution to the geochemical literature and provides better understanding of both geological and organic geochemical aspects of the Morrow Formation. As presented in this study, the Morrow has distinct biomarker characteristics that are quite different than its adjacent formations and therefore further geochemical analyses are required to address a number of unanswered questions about the Morrow.

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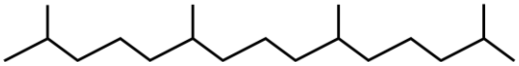
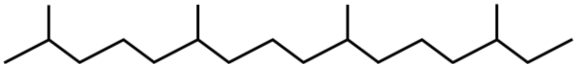
Appendix A: Compound Structures

I: C_{17} *n*-Alkane

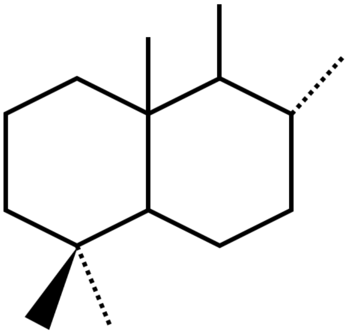
II: C_{18} *n*-Alkane



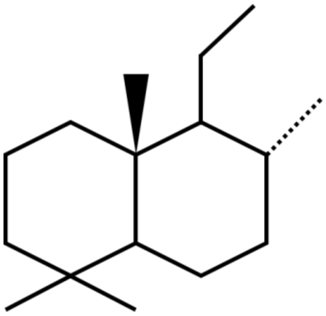
III: Pristane



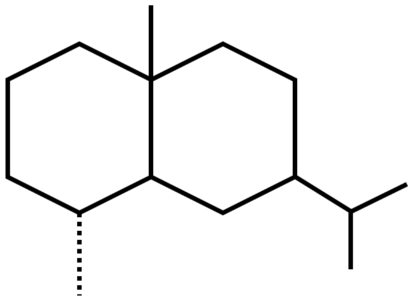
IV: Phytane



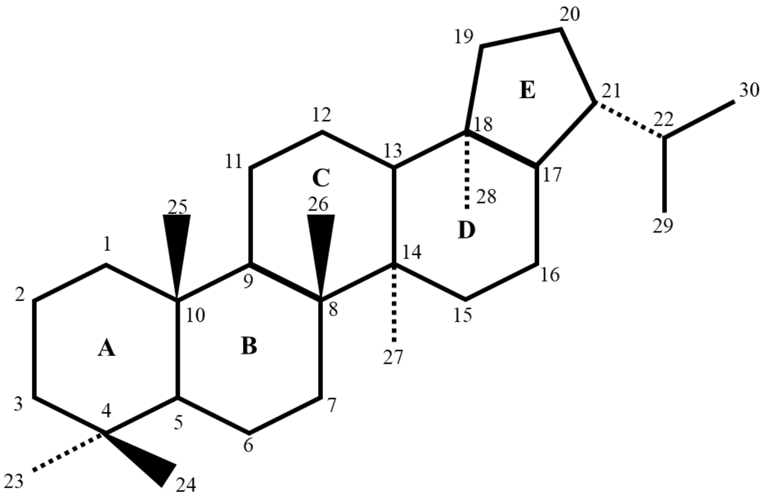
V: 8β(H)-Drimane



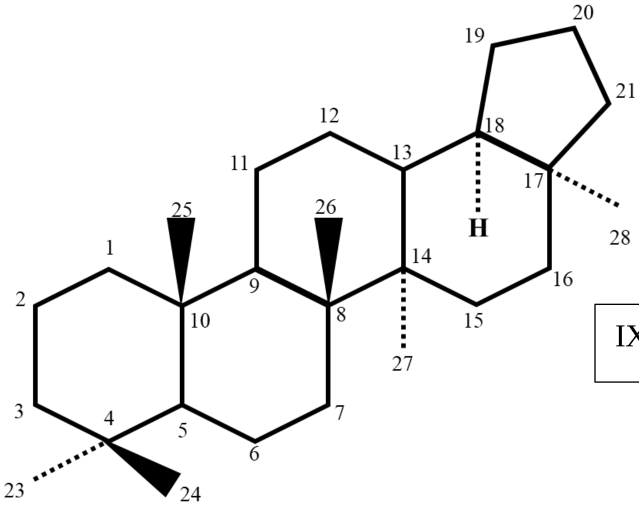
VI: 8β(H)-Homodrimane



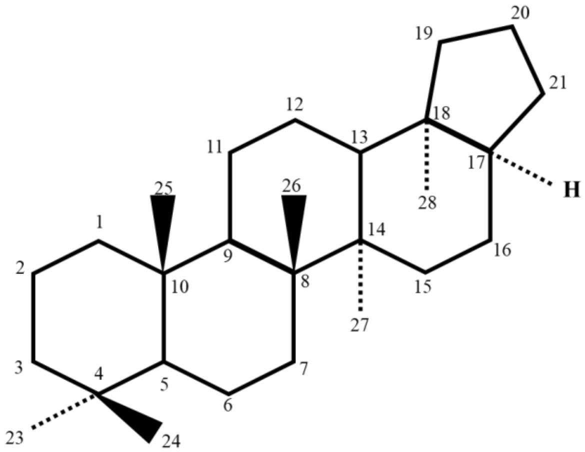
VII: 4β(H)-Eudesmane



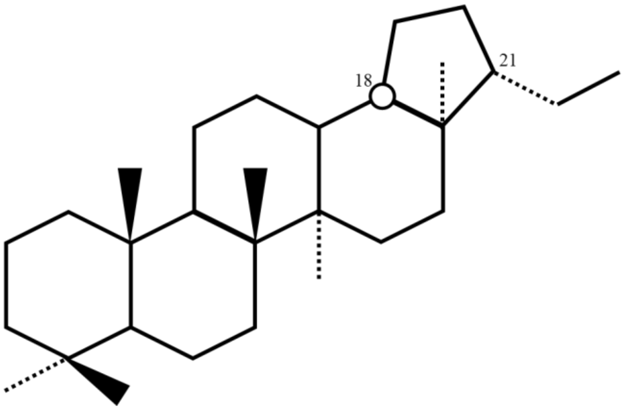
VIII: Hopane



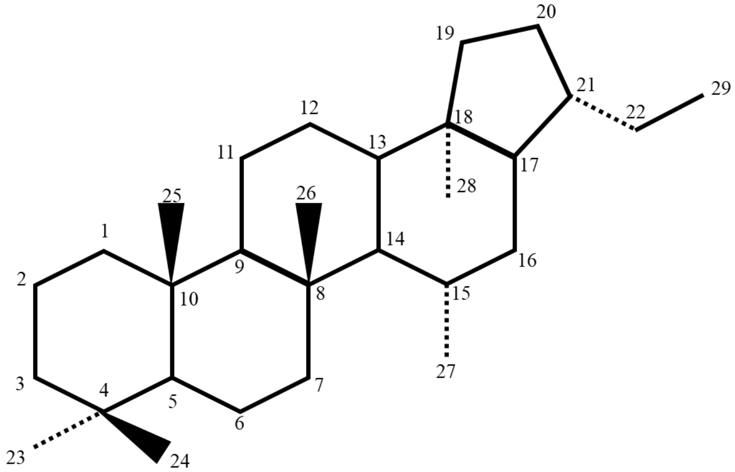
IX: 18α(H)-22,29,30 Trisnorhopane



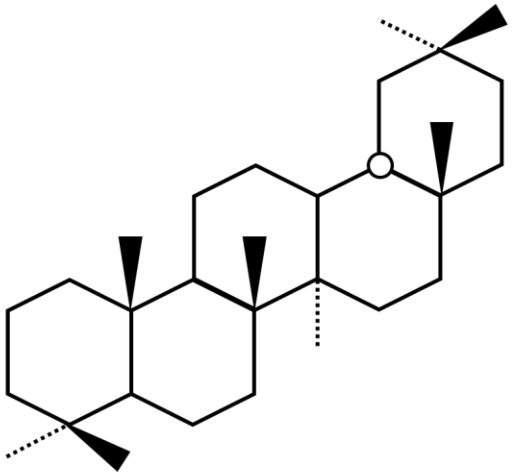
X: 17α(H)-22,29,30 Trisnorhopane



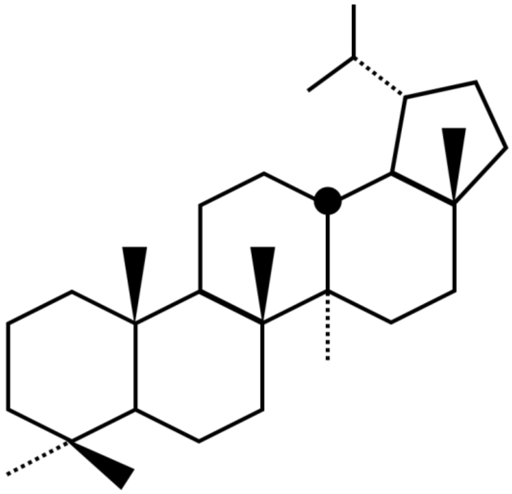
XI: C_{29} Ts



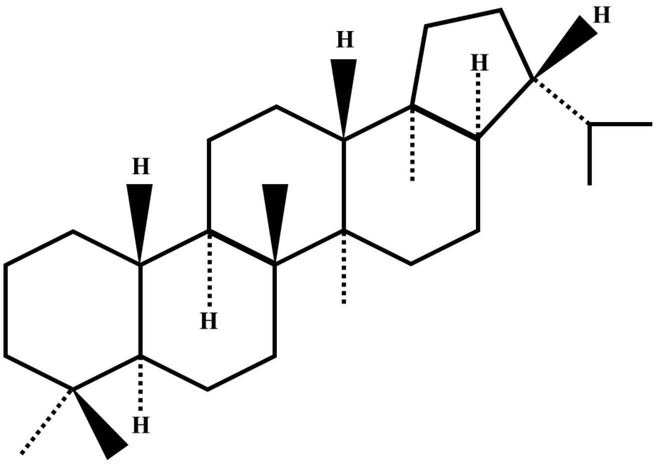
XII: 17α(H)-Diahopane



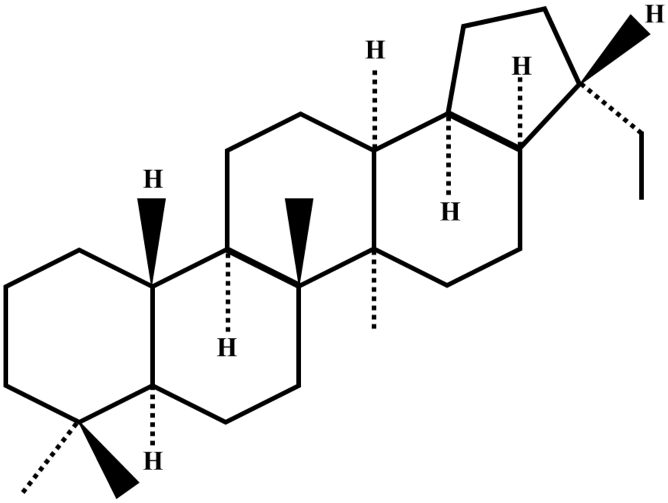
XIII: Oleanane



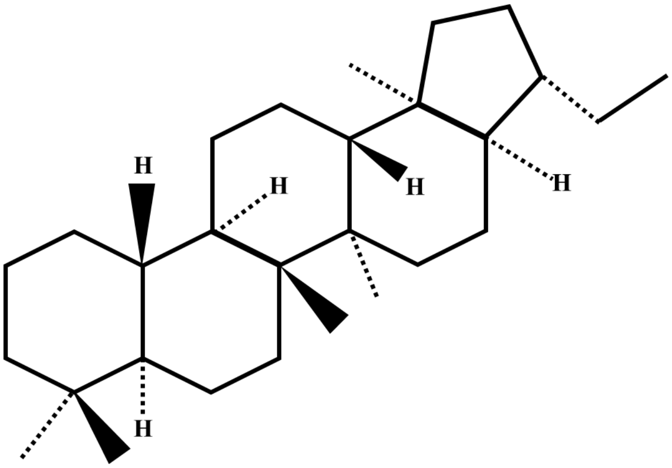
XIV: Lupane



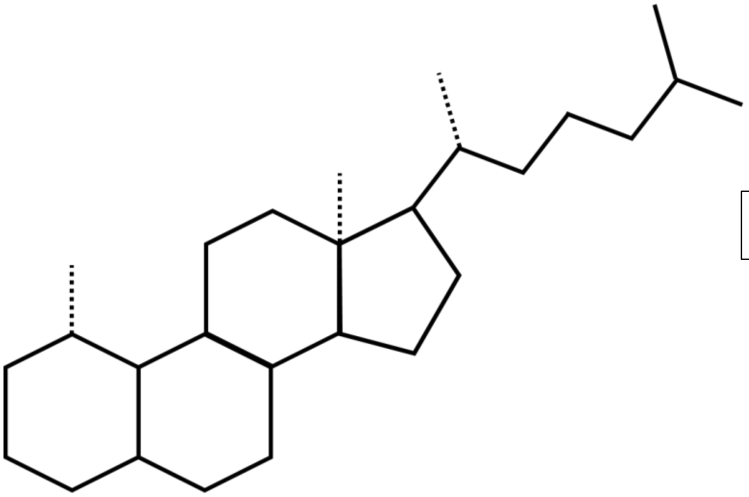
XV: 25-Norhopane



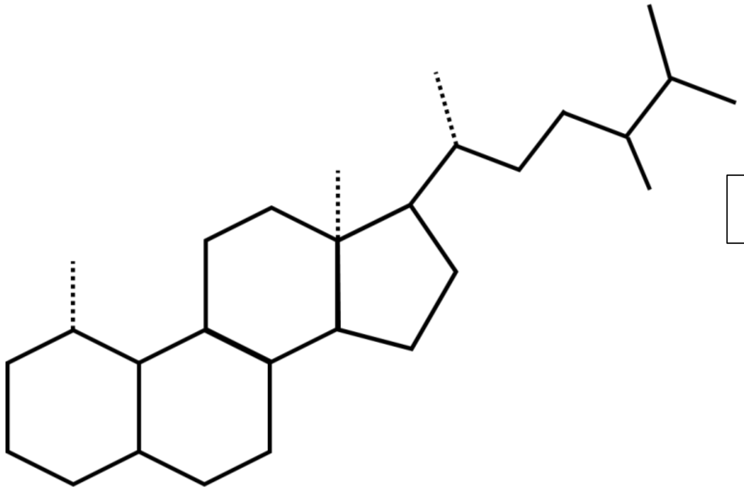
XVI: 25,28,30-Trisnorhopane



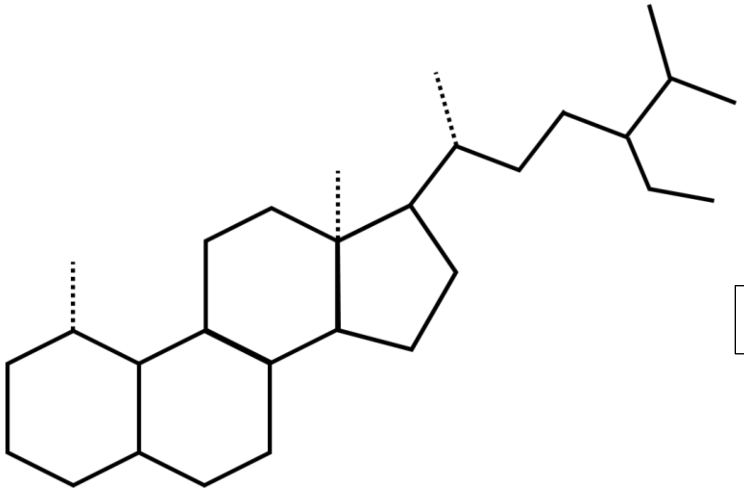
XVII: 25,30-Bisnorhopane



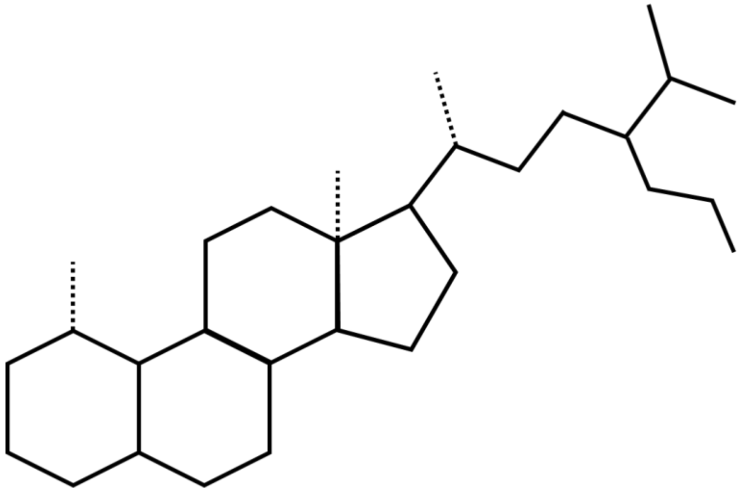
XVIII: C_{27} Steranes



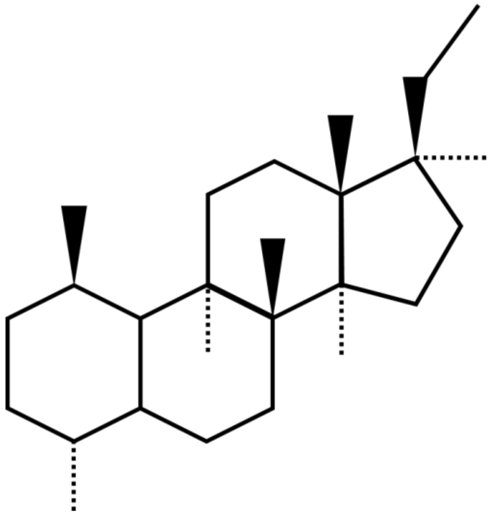
XIX: C_{28} Steranes



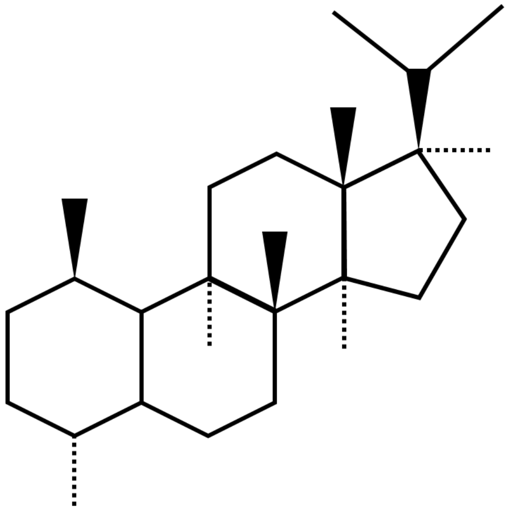
XX: C_{29} Steranes



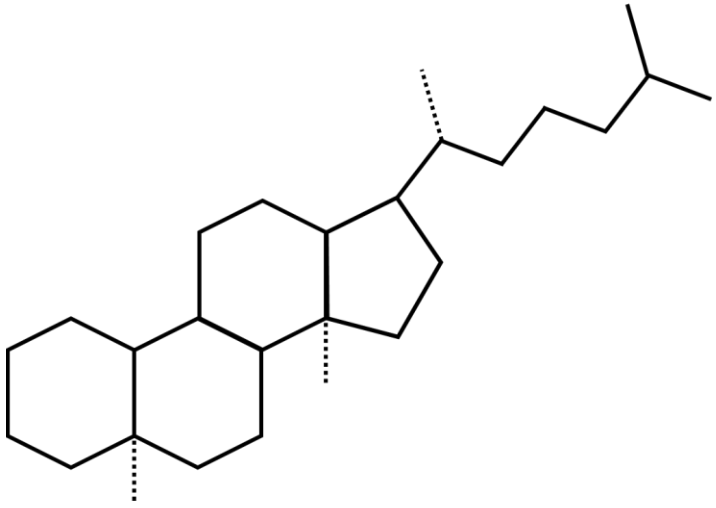
XXI: C_{30} Steranes



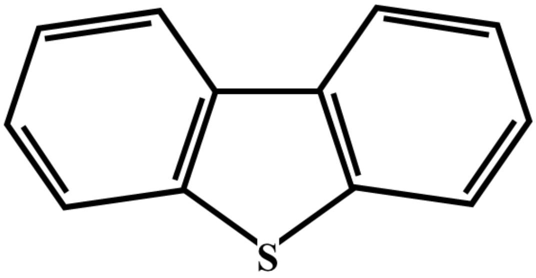
XXII: Pregnane



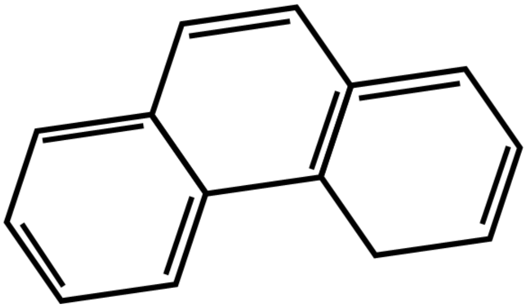
XXIII: Homopregnane



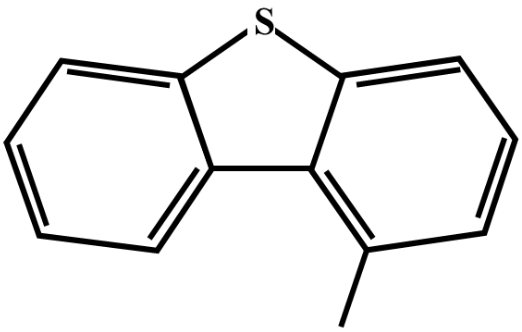
XXIV: C_{27} Diasterane



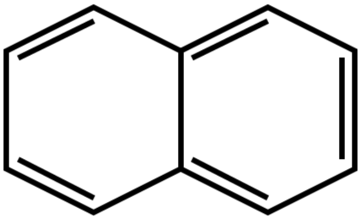
XXV: Dibenzothiophene



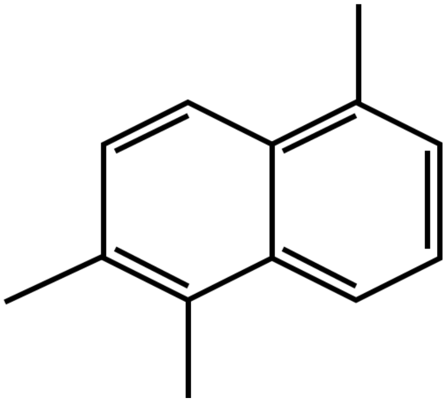
XXVI: Phenanthrene



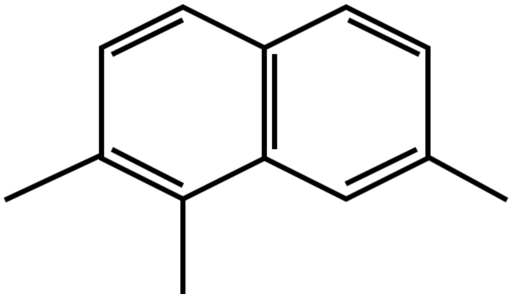
XXVII: MTBT



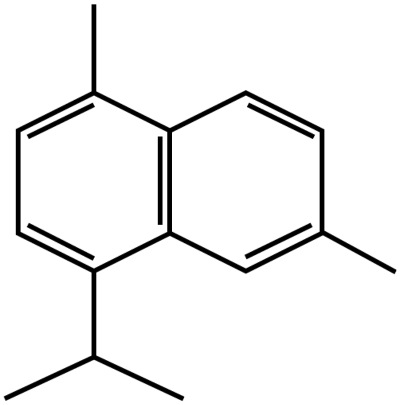
XXVIII: Naphthalene



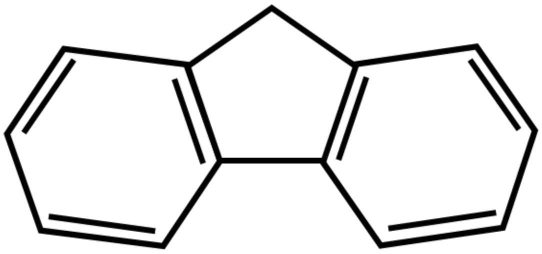
XXIX: 1,2,5-TMN



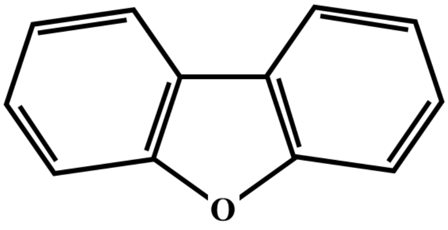
XXX: 1,2,7-TMN



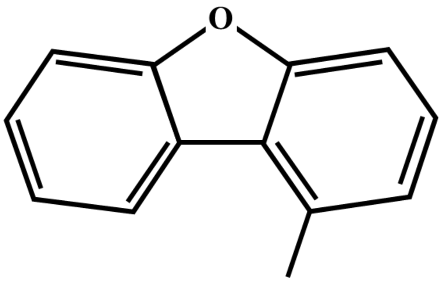
XXXI: Cadalene



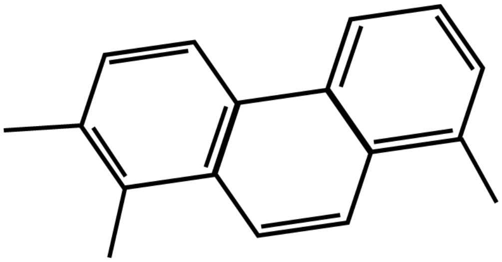
XXXII: Fluorene



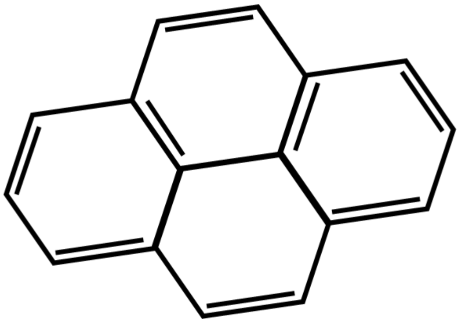
XXXIII: Dibenzofuran



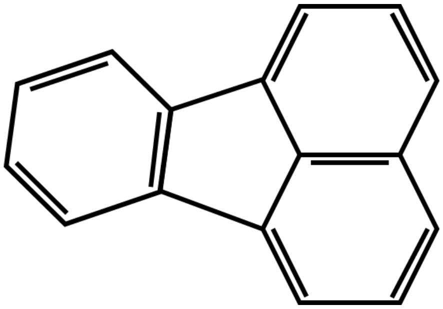
XXXIV: Methyldibenzofuran



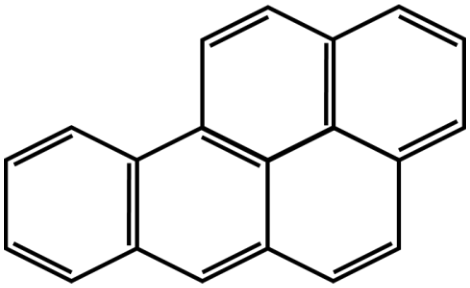
XXXV: 1,2,8-TMP



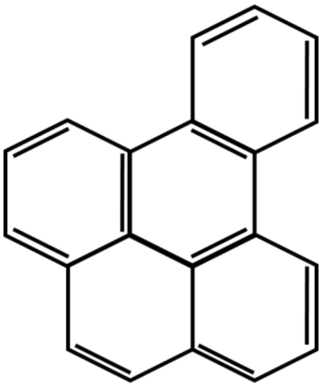
XXXVI: Pyrene



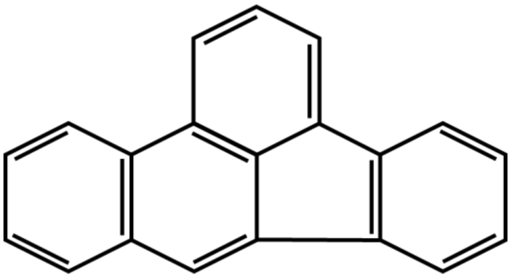
XXXVII: Fluoranthene



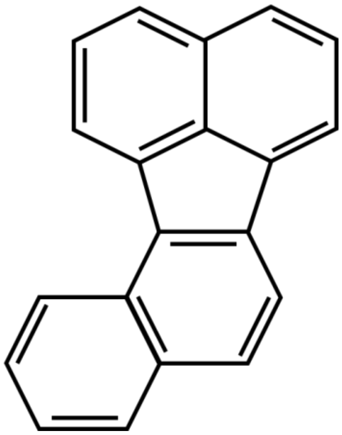
XXXVIIIa: Benzo(a)pyrene



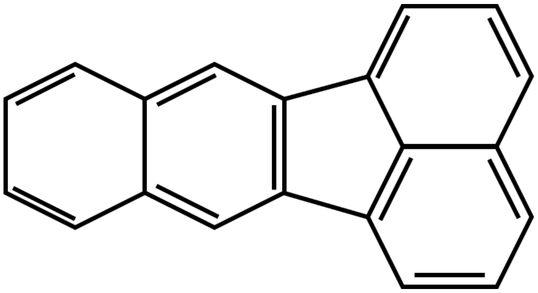
XXXVIIIb: Benzo(e)pyrene



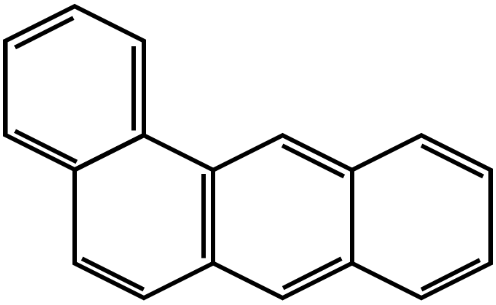
XXXIXa: Benzo(b)fluoranthene



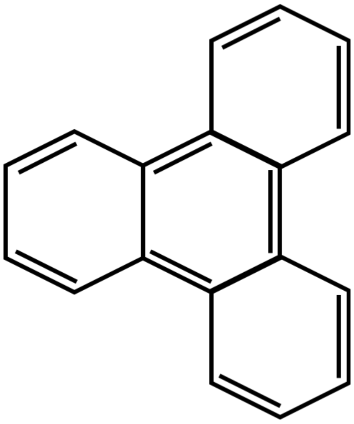
XXXIXb: Benzo(j)fluoranthene



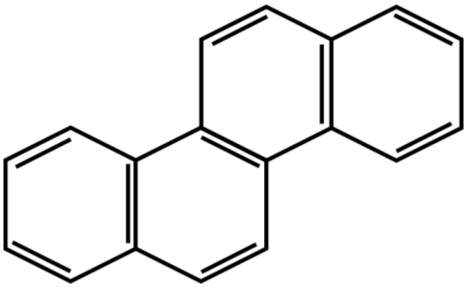
XXXIXc: Benzo(k)fluoranthene



XL: Benzoanthracene



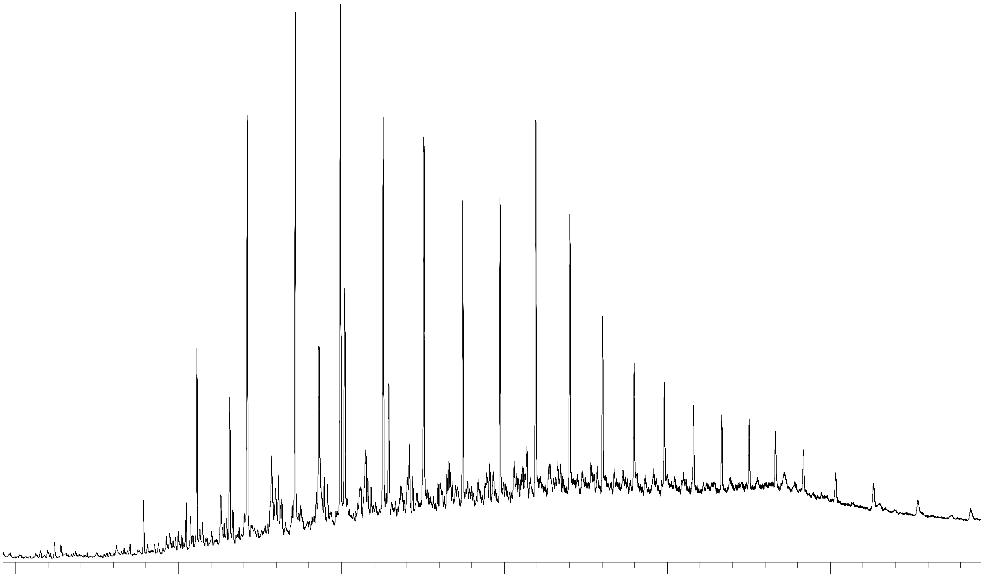
XLI: Triphenylene



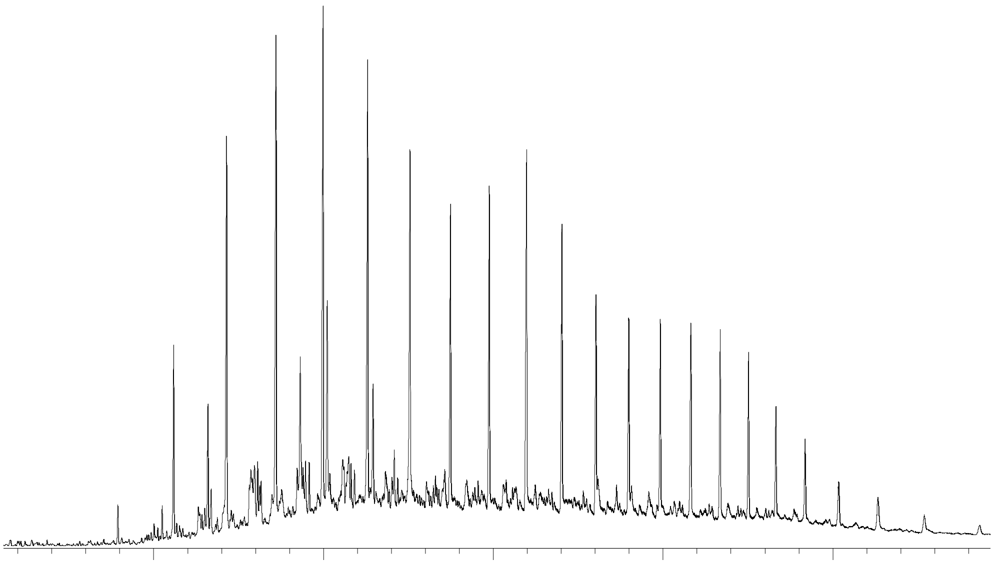
XLII: Chrysene

Appendix B: Selected Gas Chromatography Results

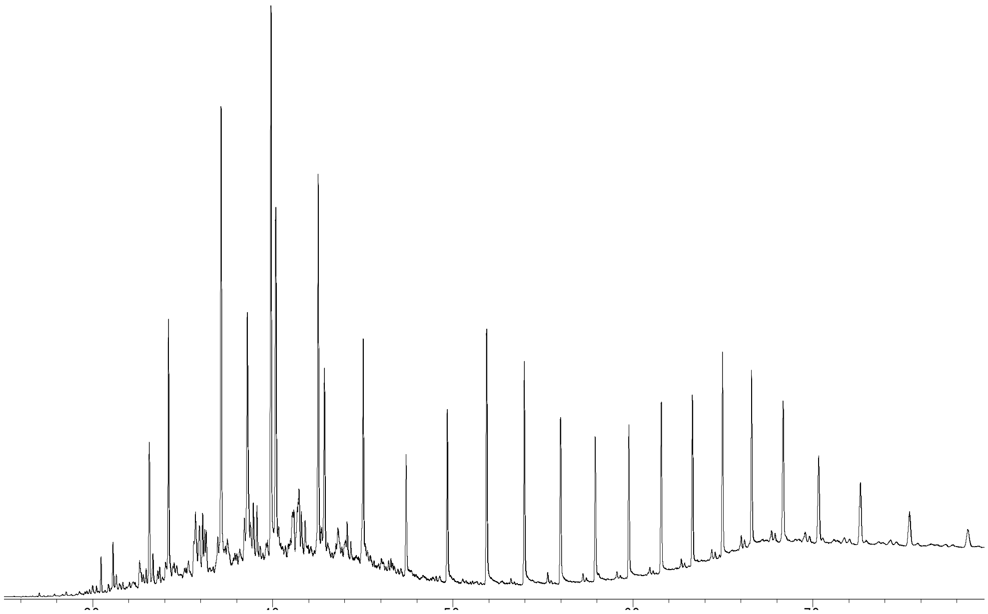
MOR-68



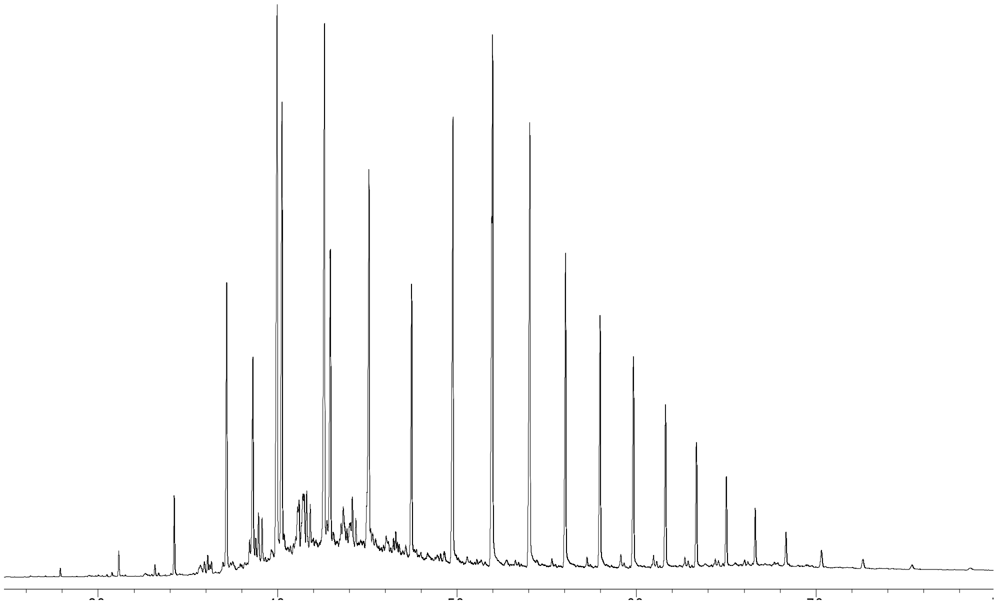
MOR-86



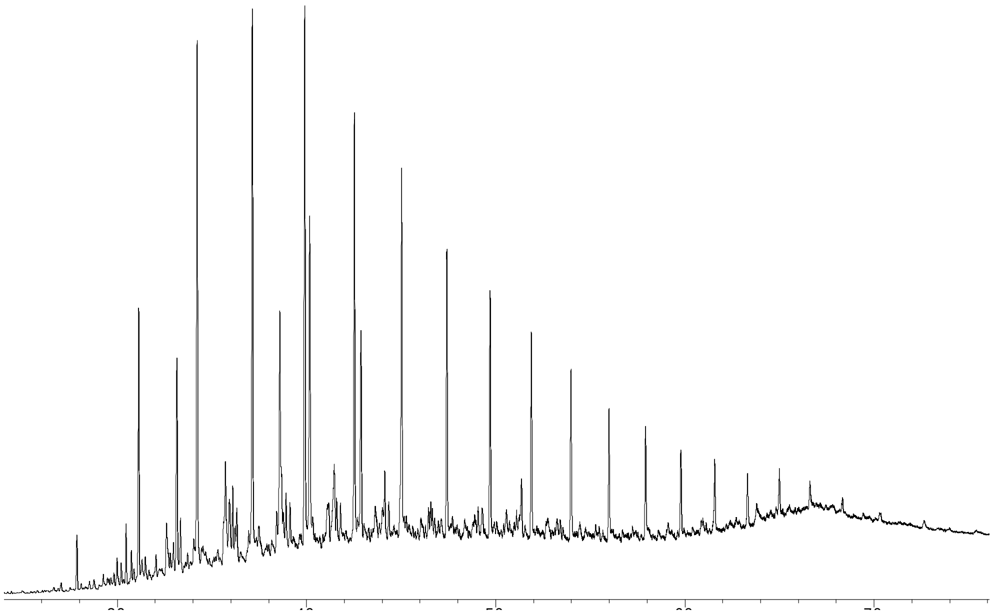
MOR-33



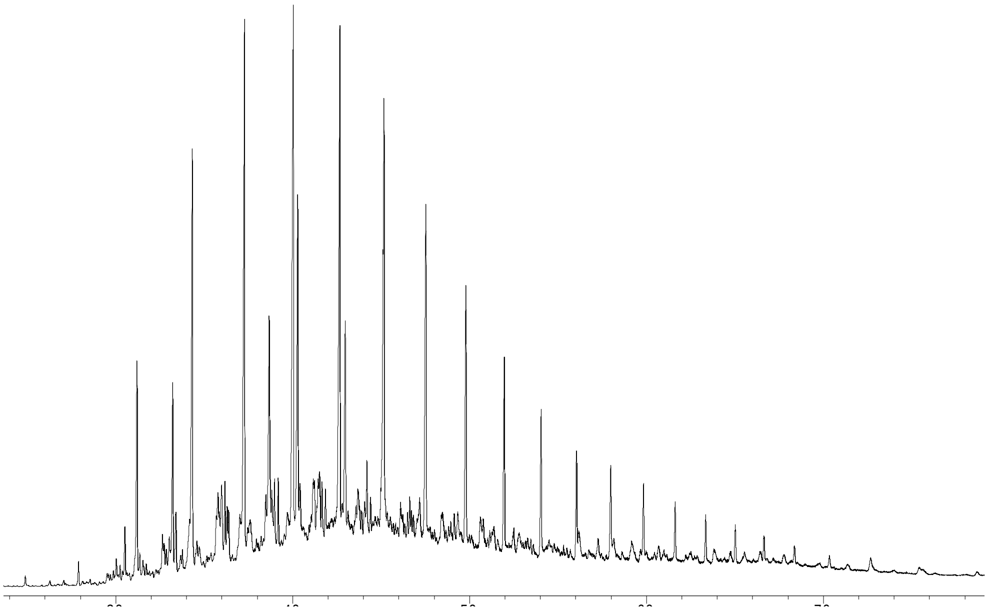
MOR-16



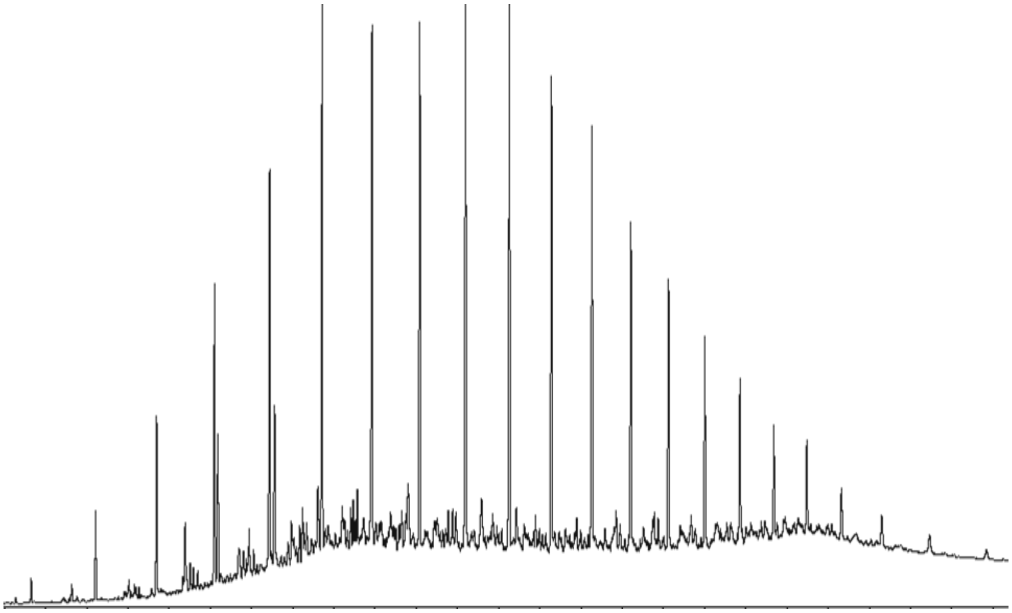
MOR-66



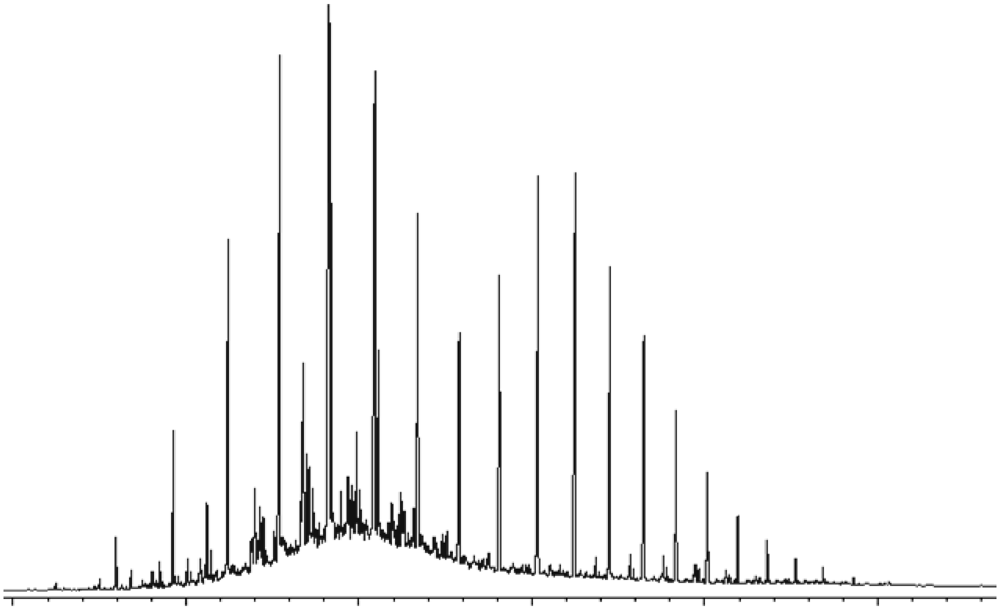
MOR-2



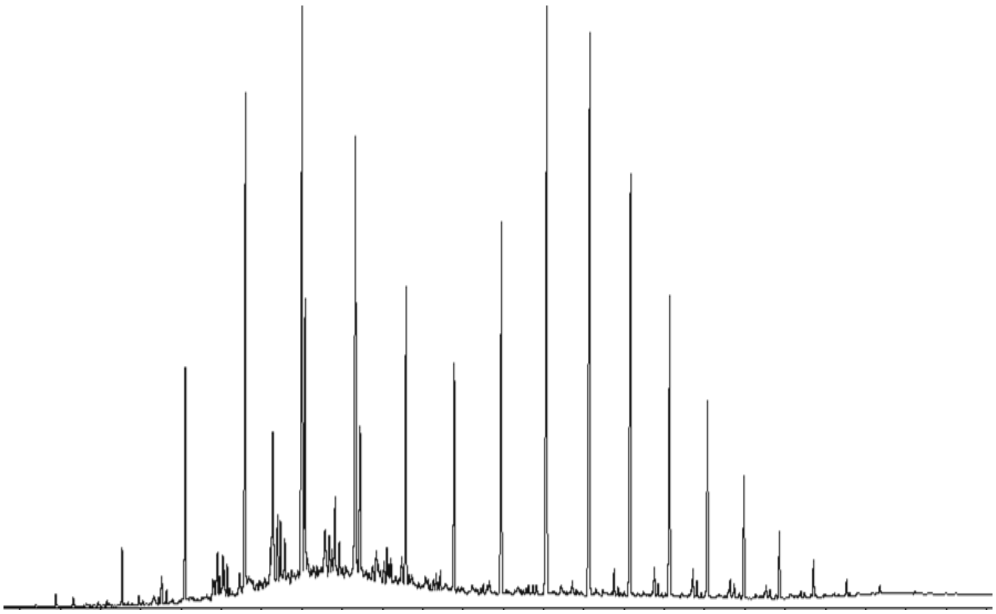
A-11



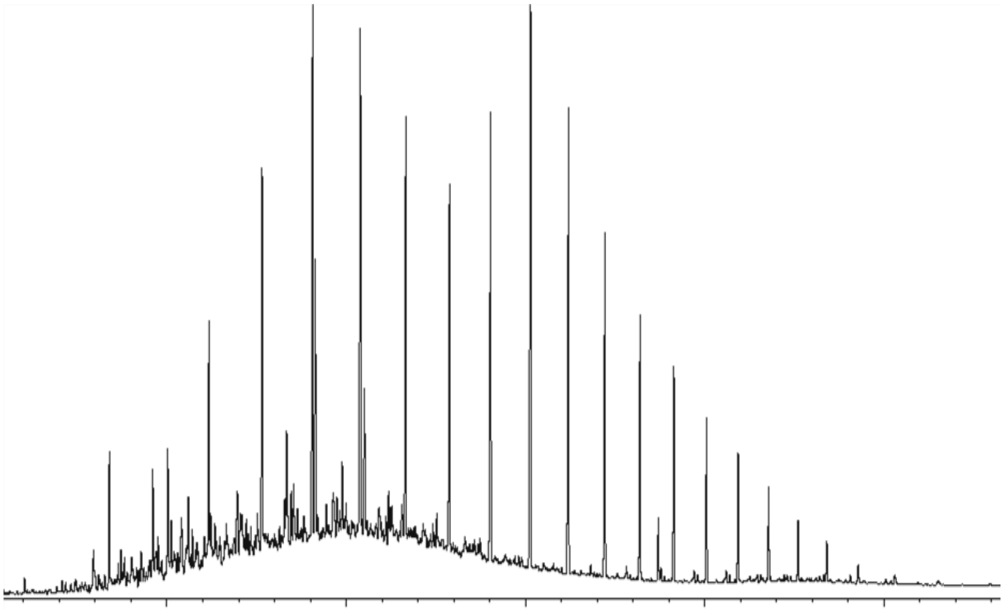
A-22



A-28

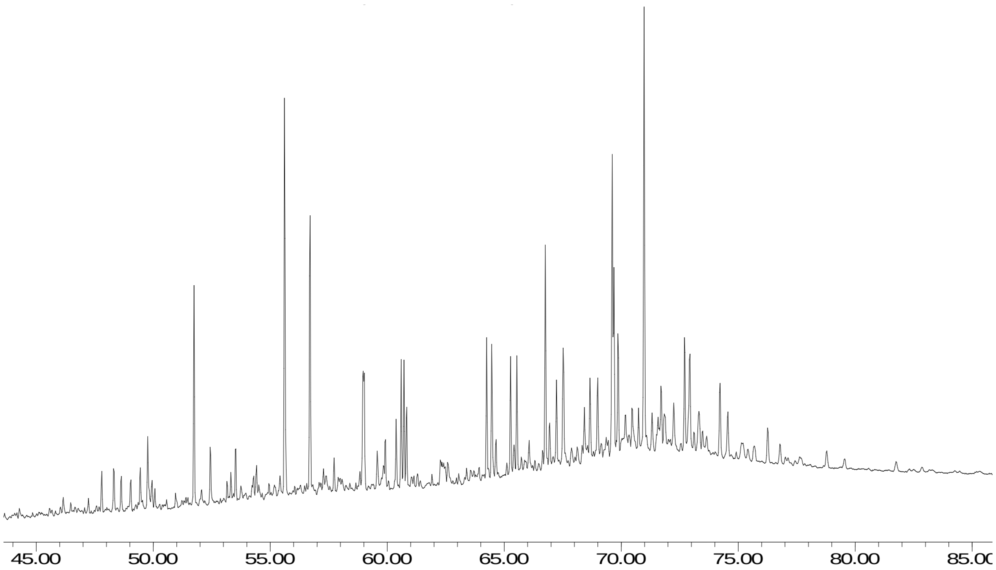


H-3

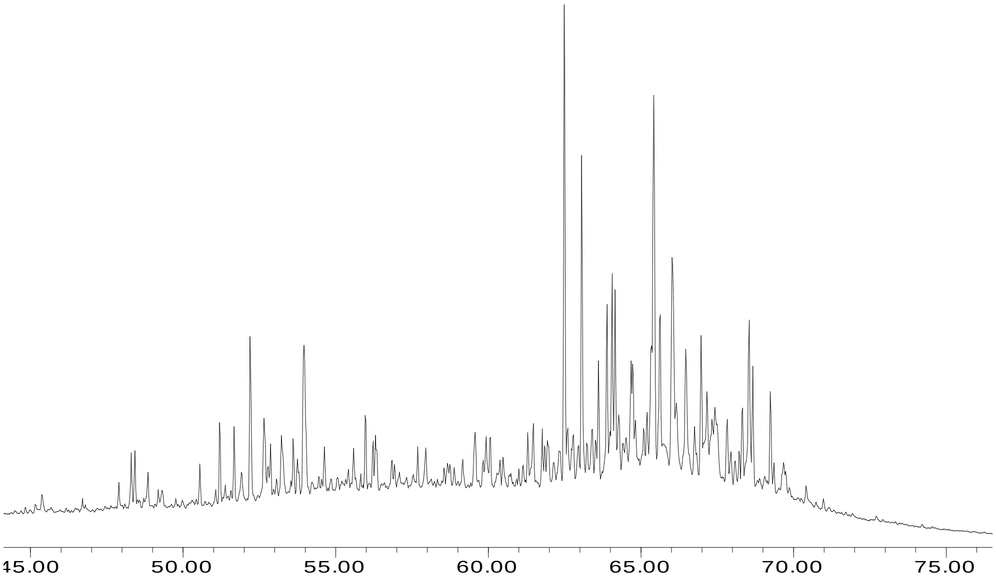


Appendix C: Selected GCMS Results

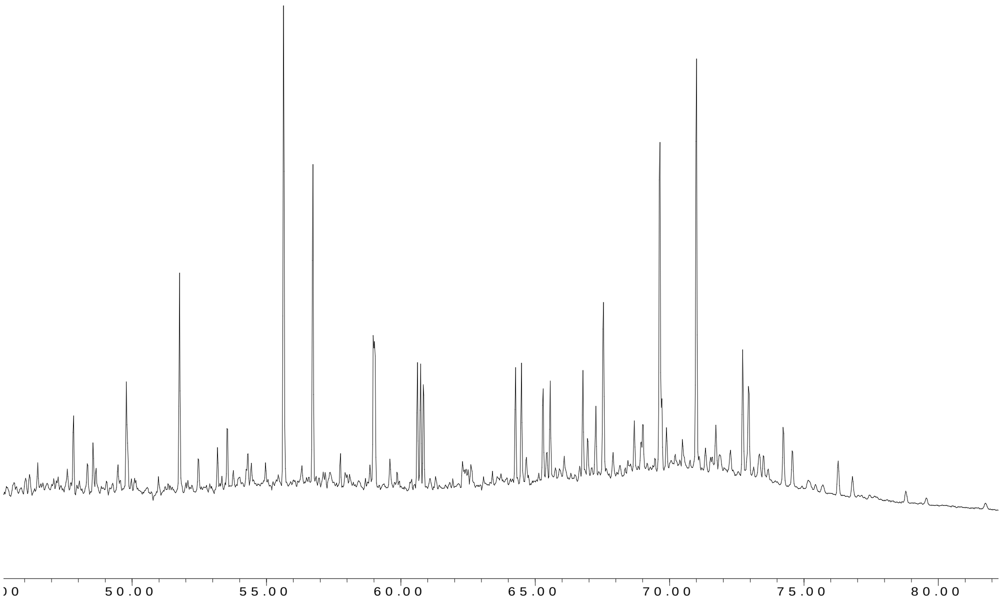
MOR-68 (191.3)



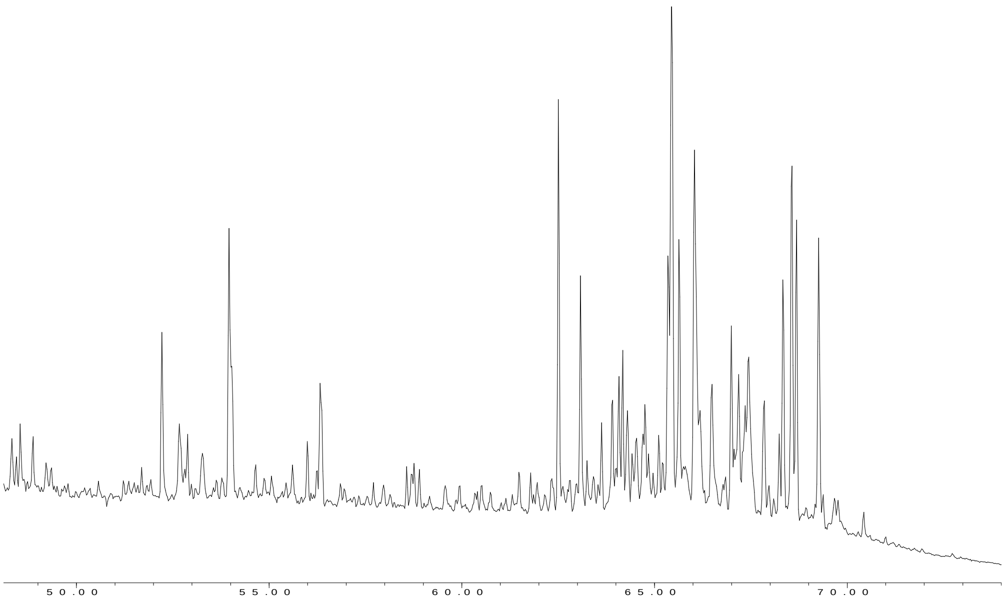
MOR-68 (217.3)



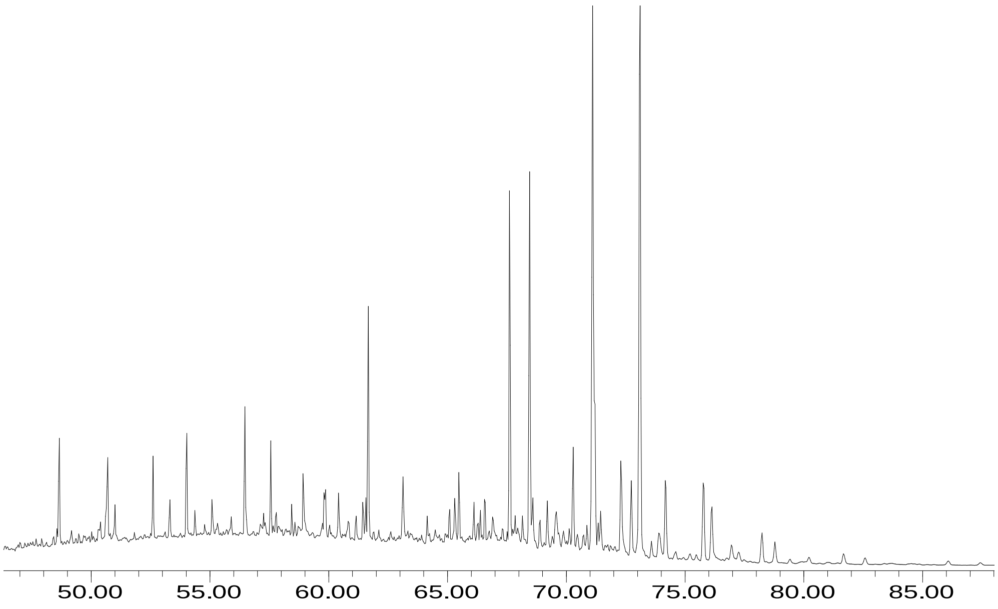
MOR-86 (191.3)



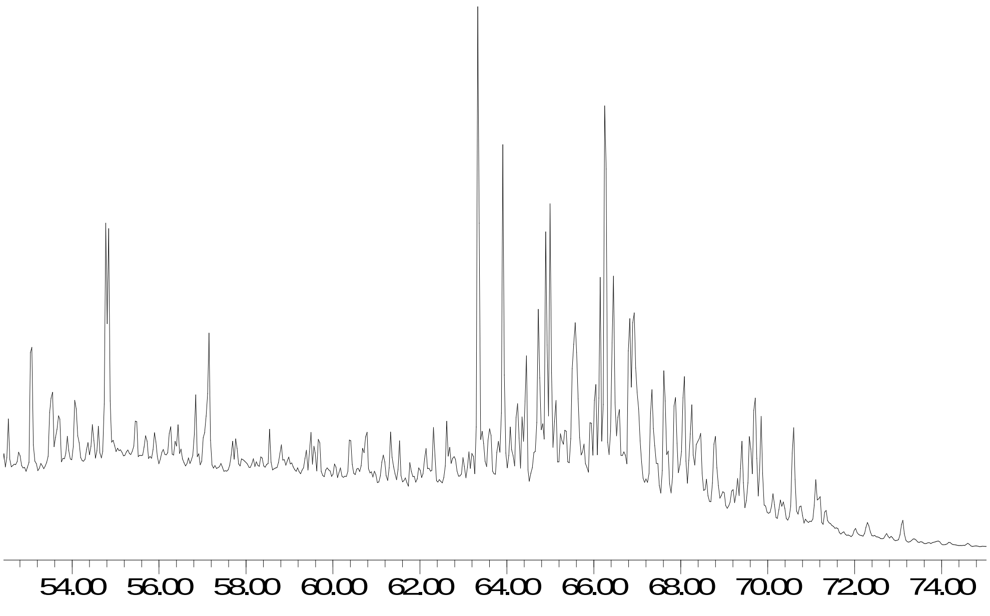
MOR-86 (217.3)



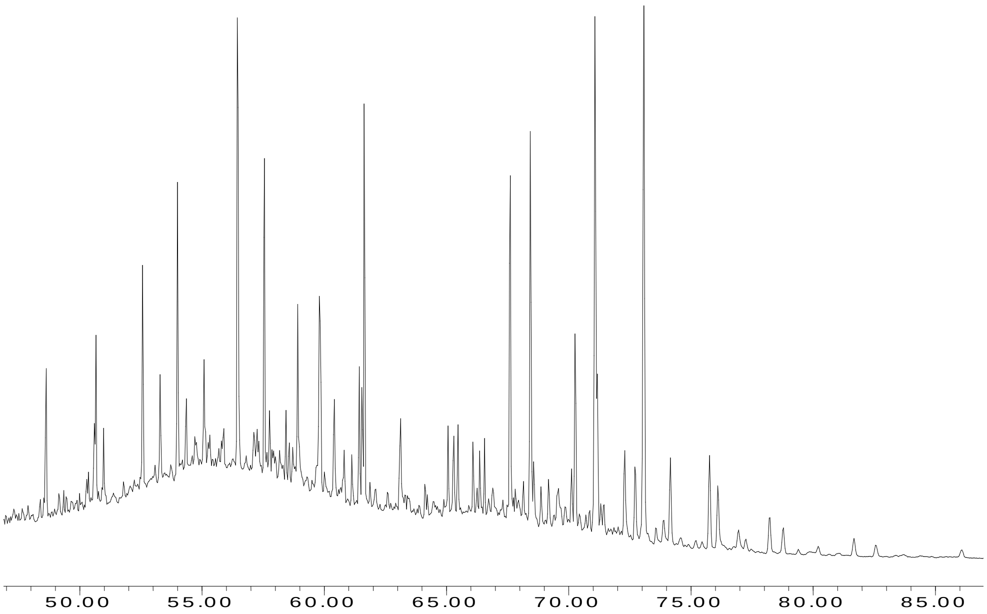
MOR-57 (191.3)



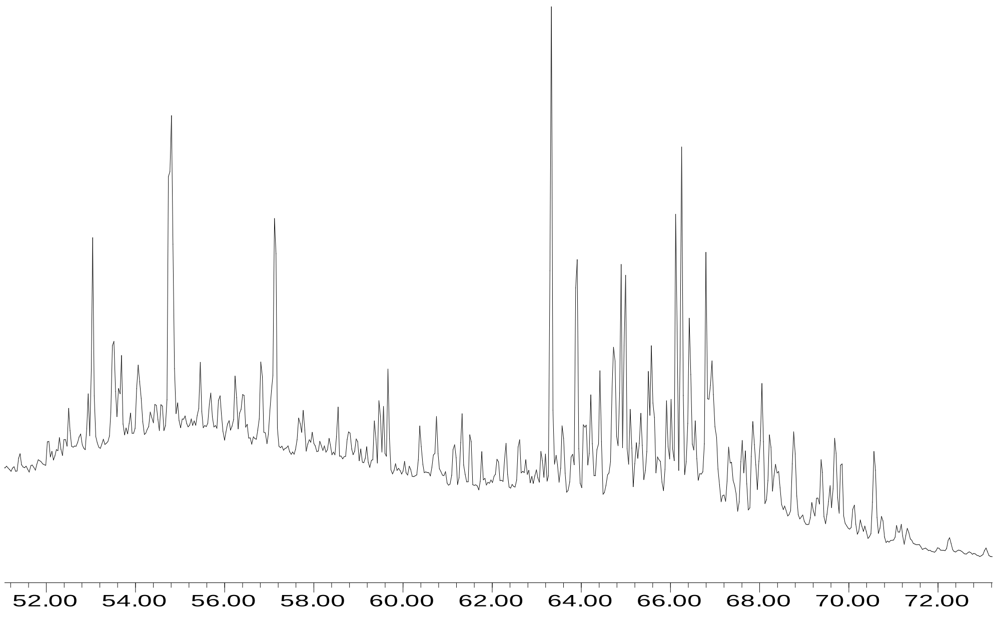
MOR-57 (217.3)



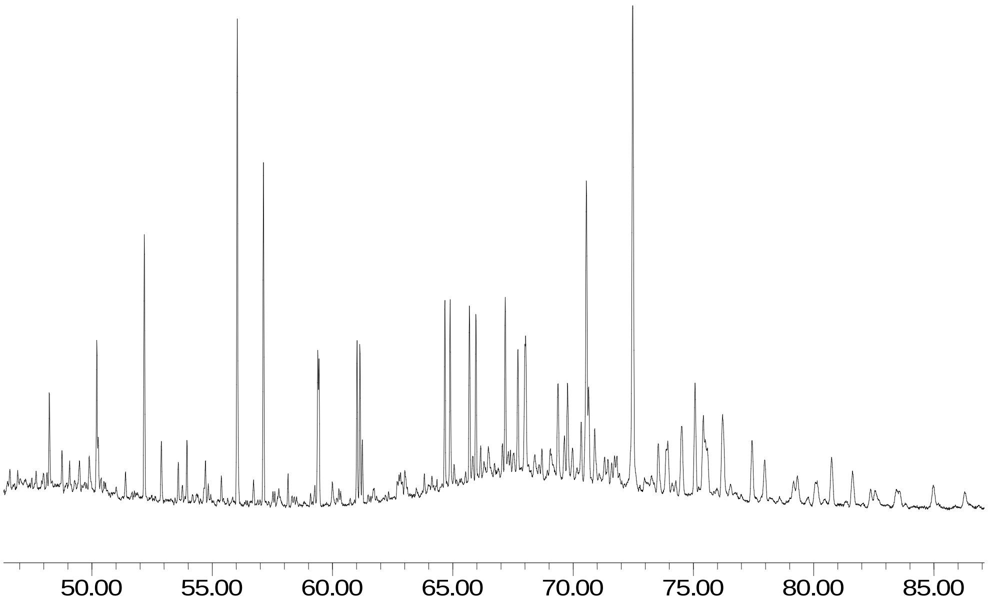
MOR-74 B/C (191.3)



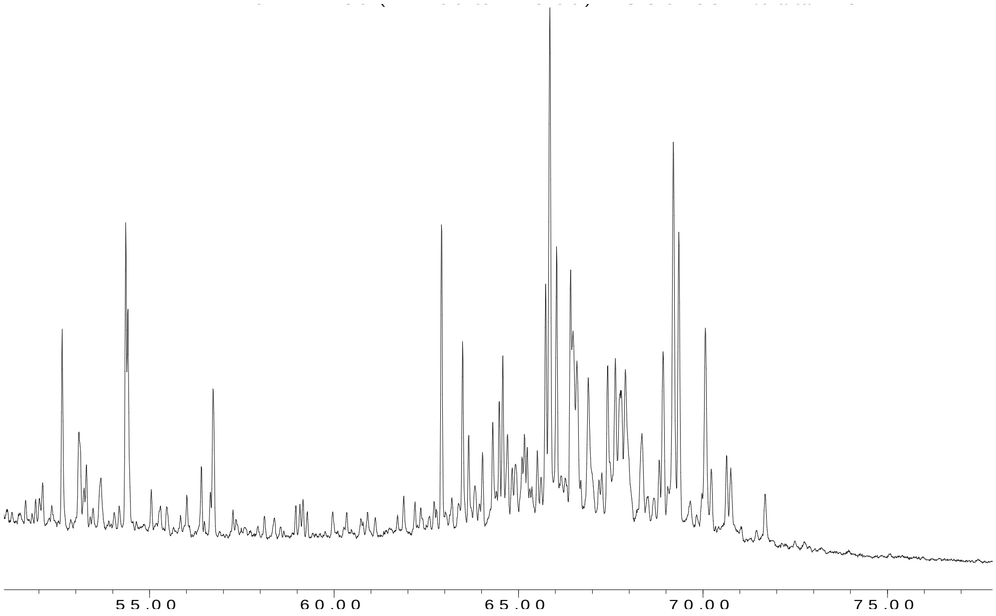
MOR-74 (217.3)



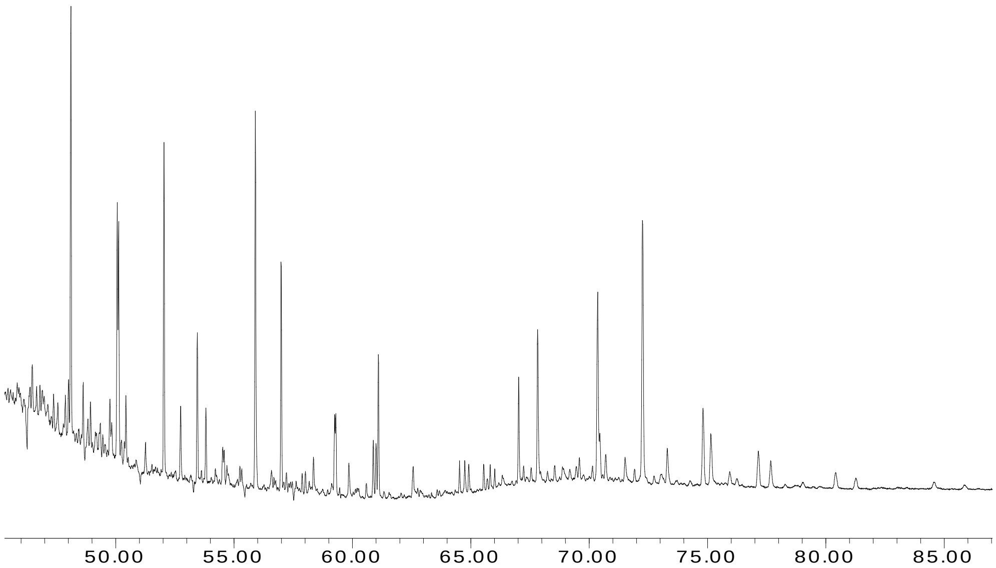
A-8 (191.3)



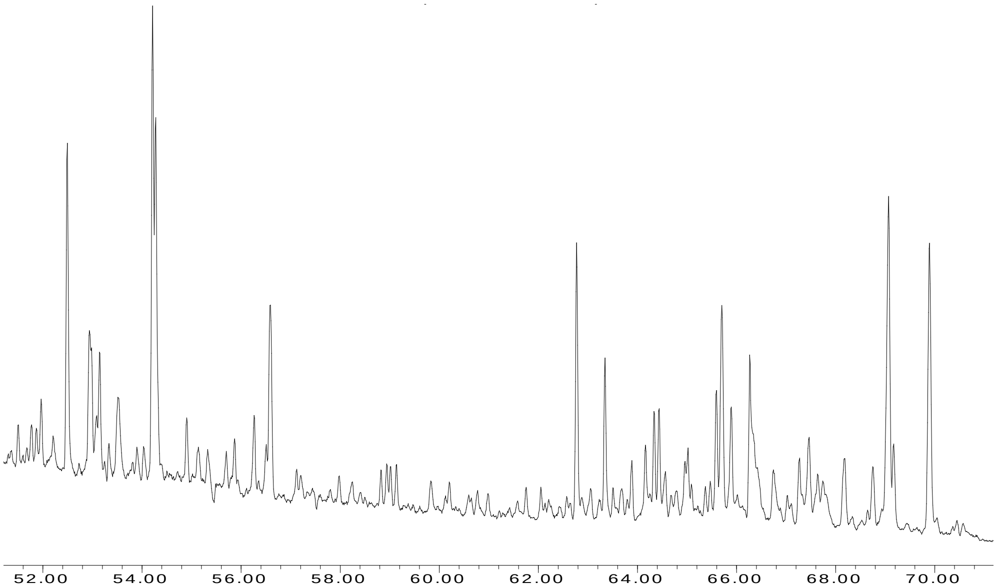
A-8 (217.3)



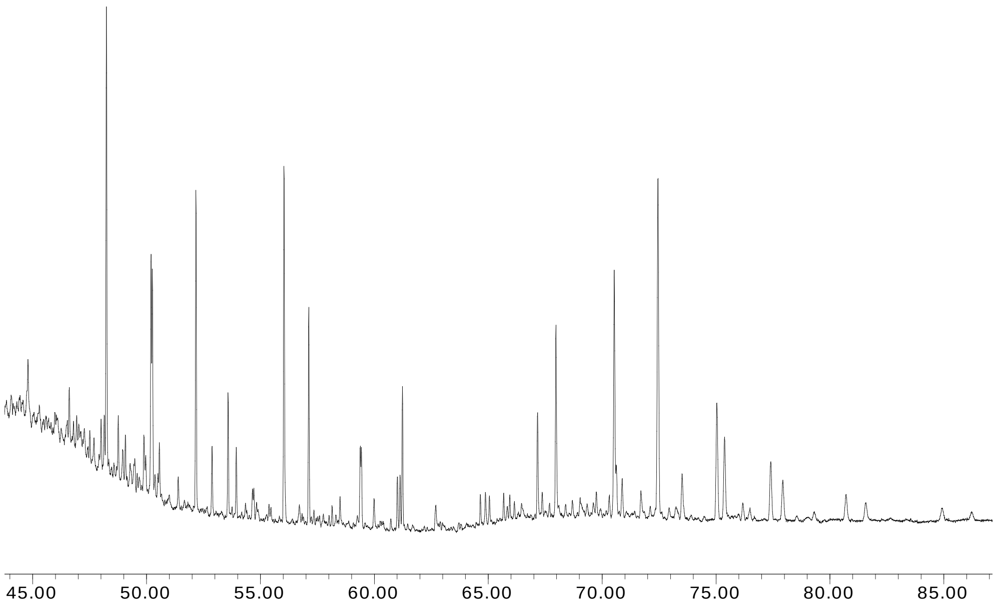
A-16 (191.3)



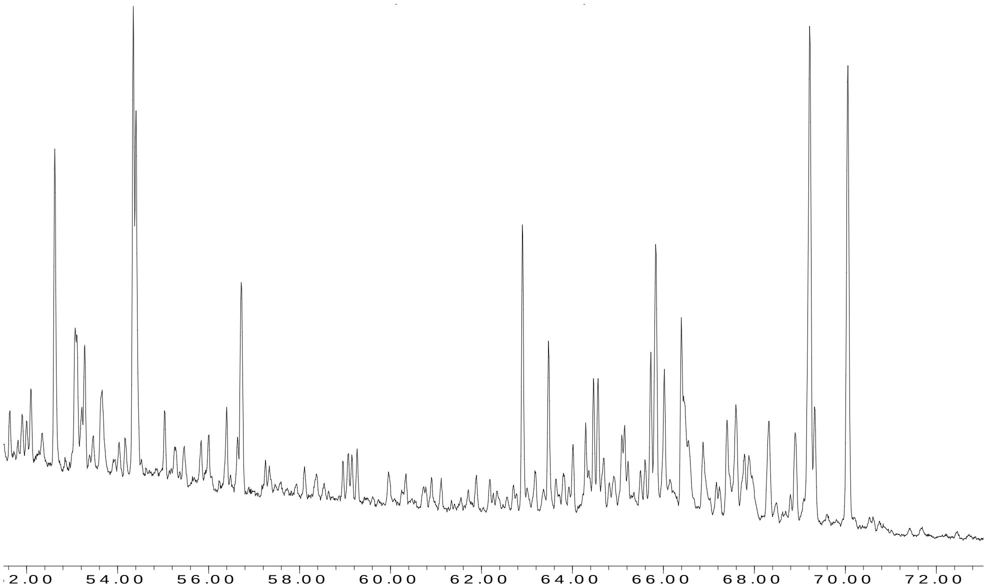
A-16 (217.3)



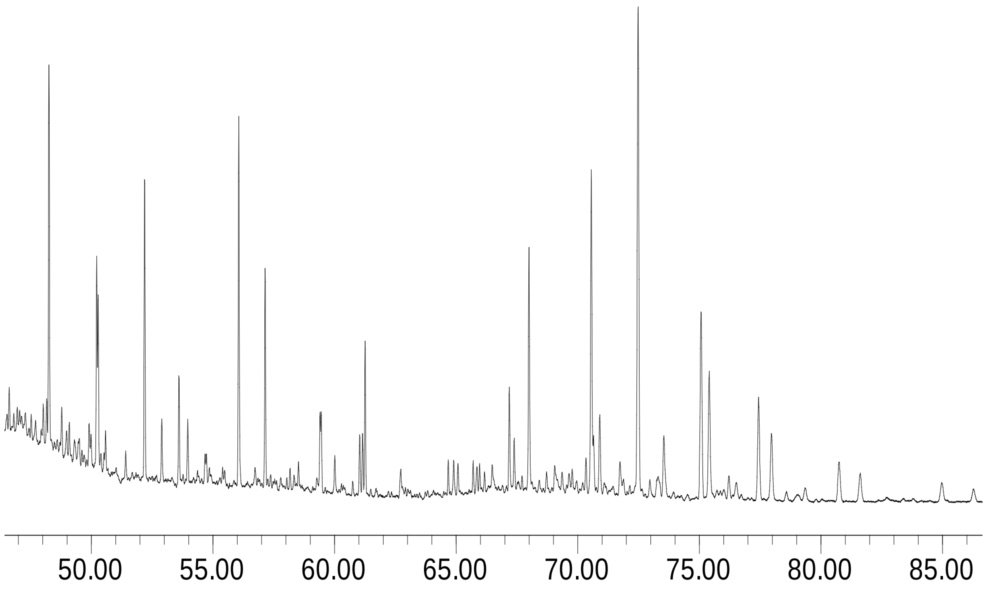
A-20 (191.3)



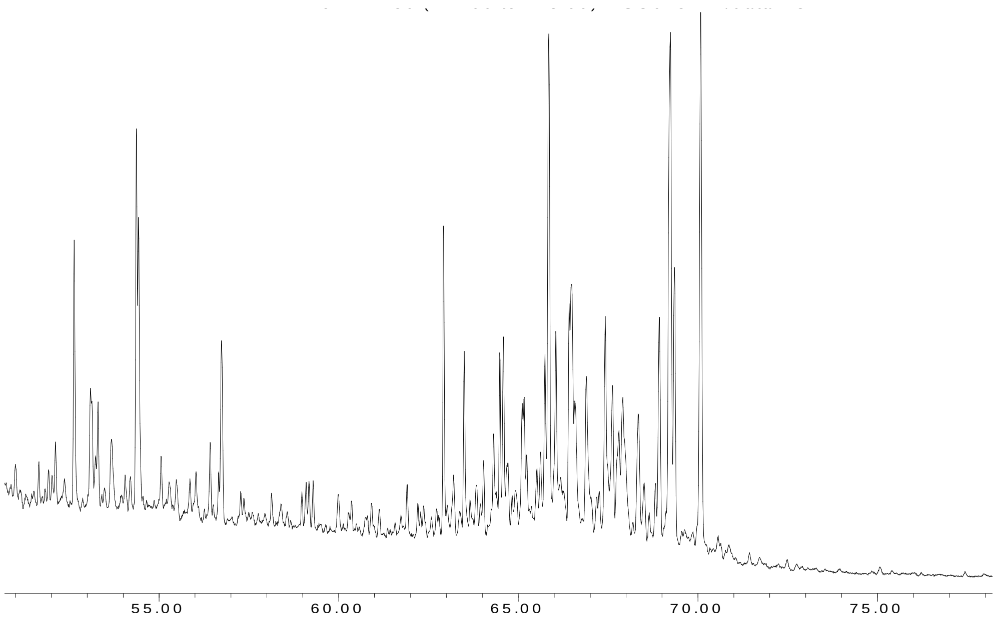
A-20 (217.3)



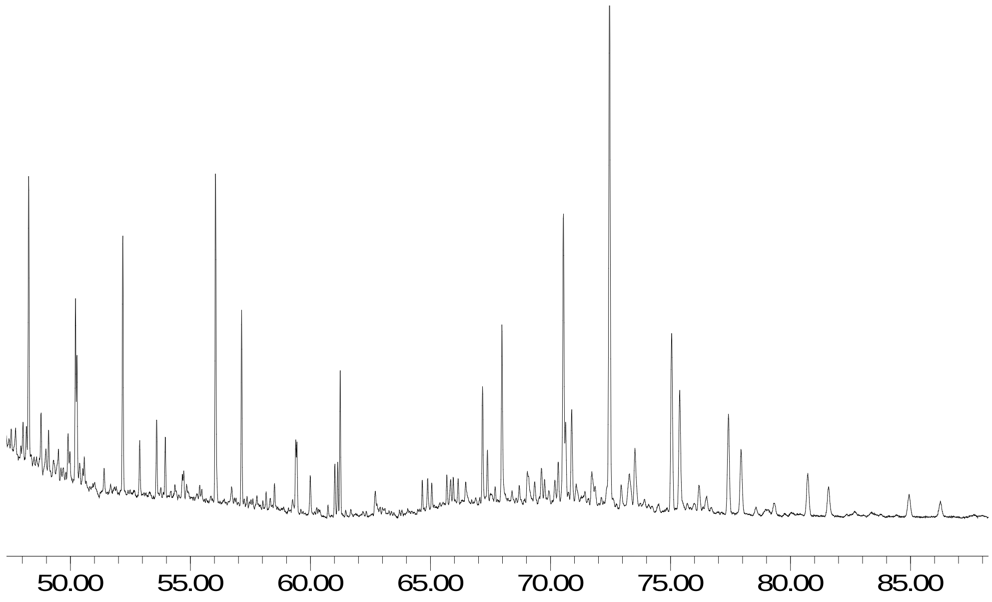
A-22 (191.3)



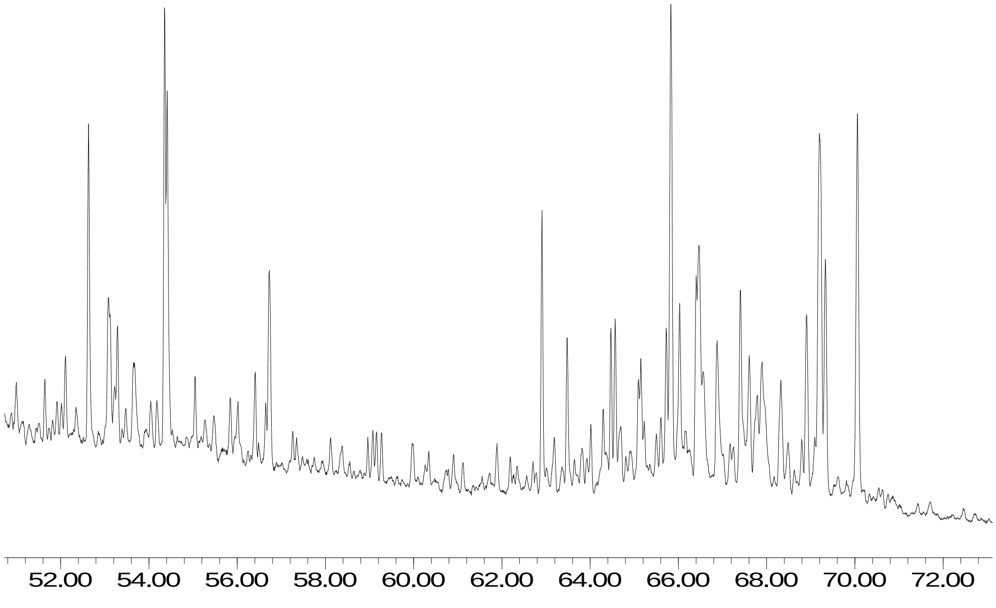
A-22 (217.3)



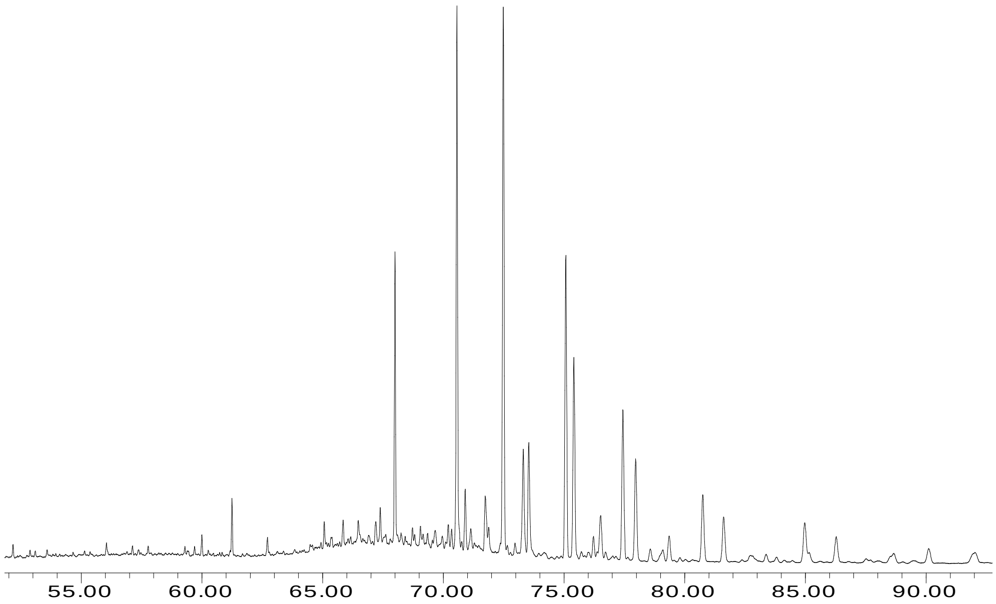
A-26 (191.3)



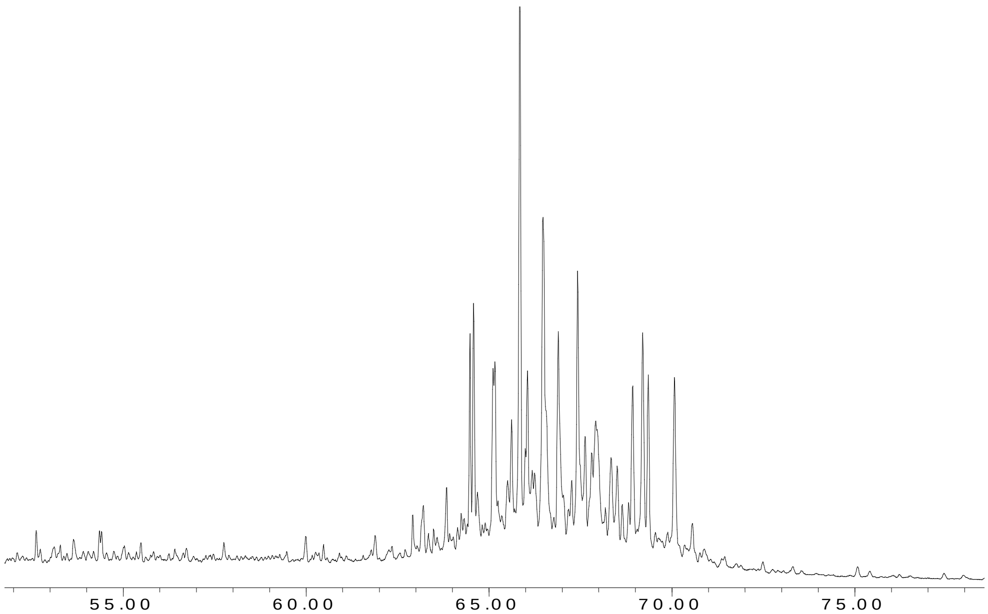
A-26 (217.3)



H-2 (191.3)

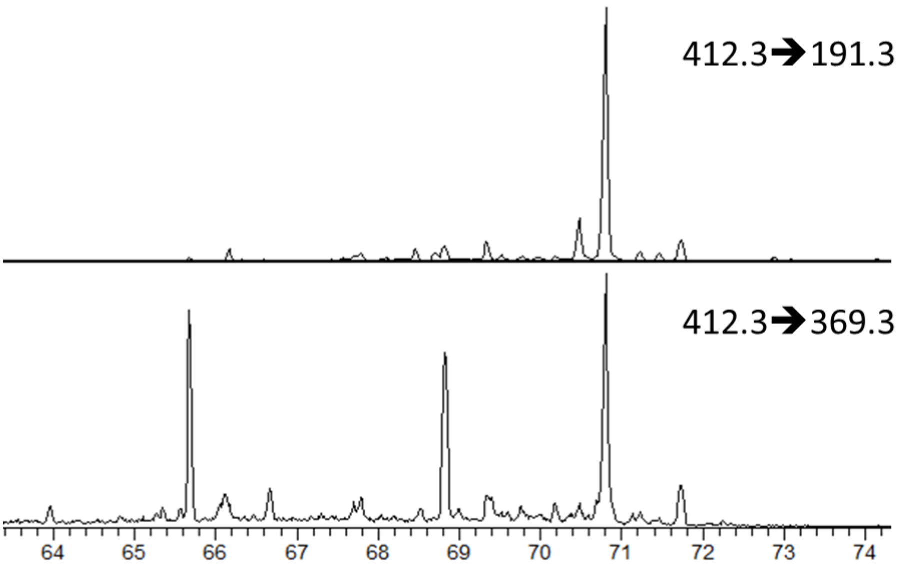


H-2 (217.3)

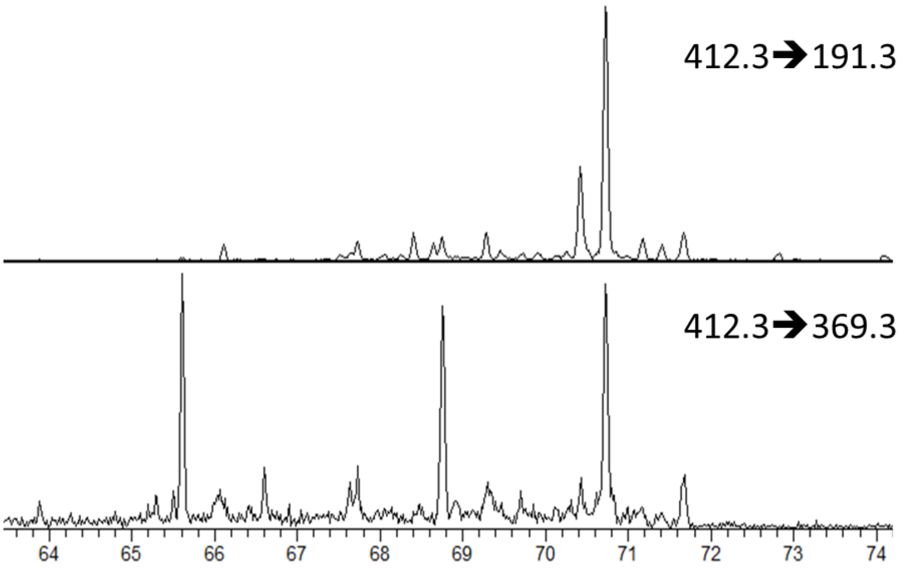


Appendix D: Selected GCMS-MS Results

MOR-57

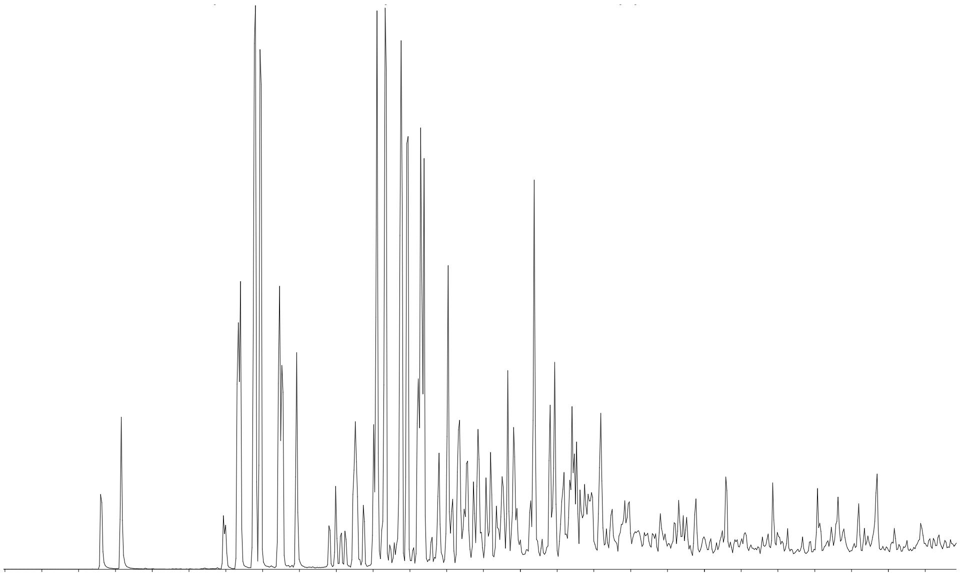


MOR-74

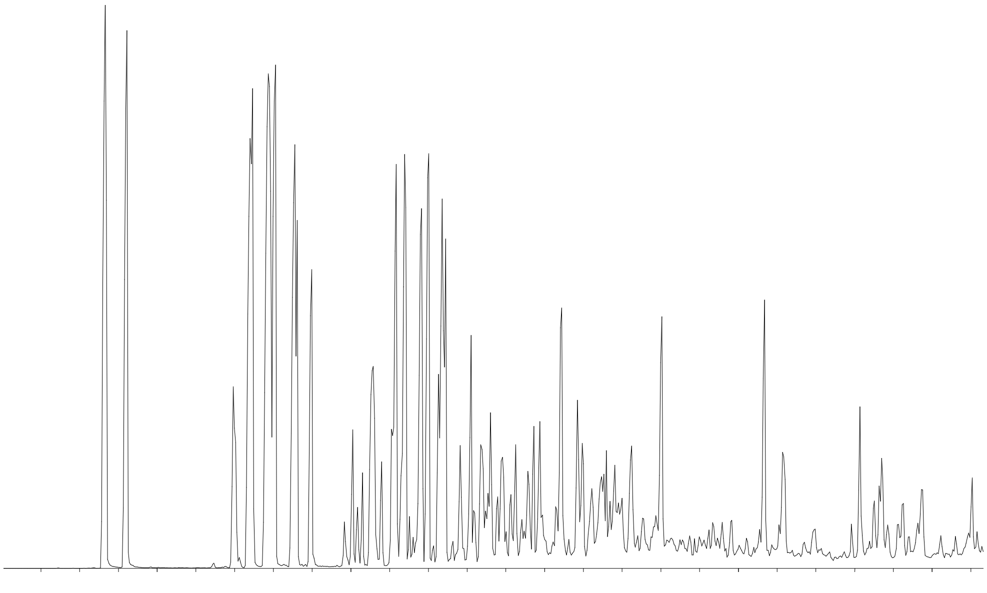


Appendix E: Naphthalene Distribution of Selected Samples

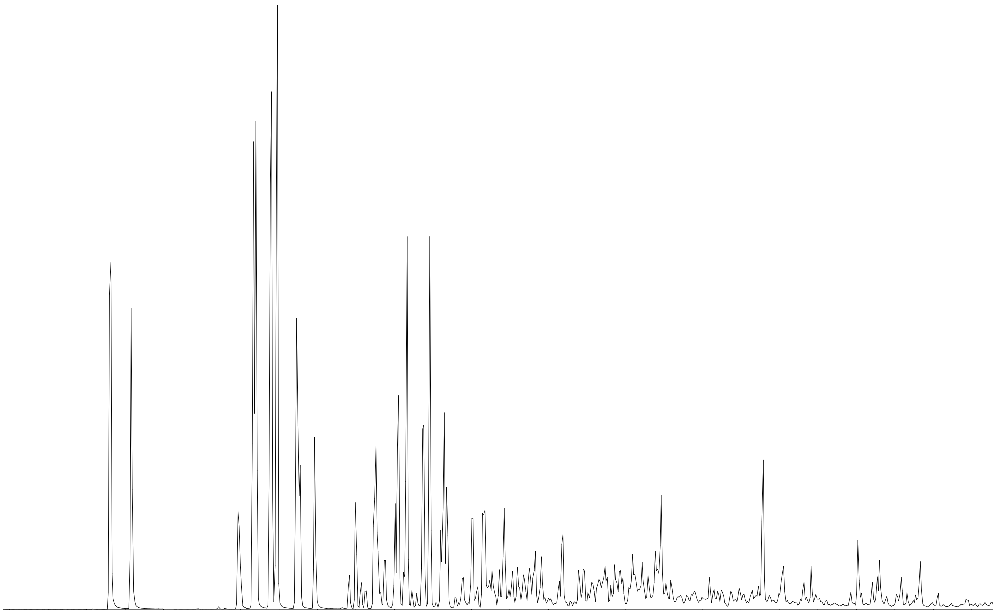
MOR-66 (m/z 142+156+170+184+198+212)



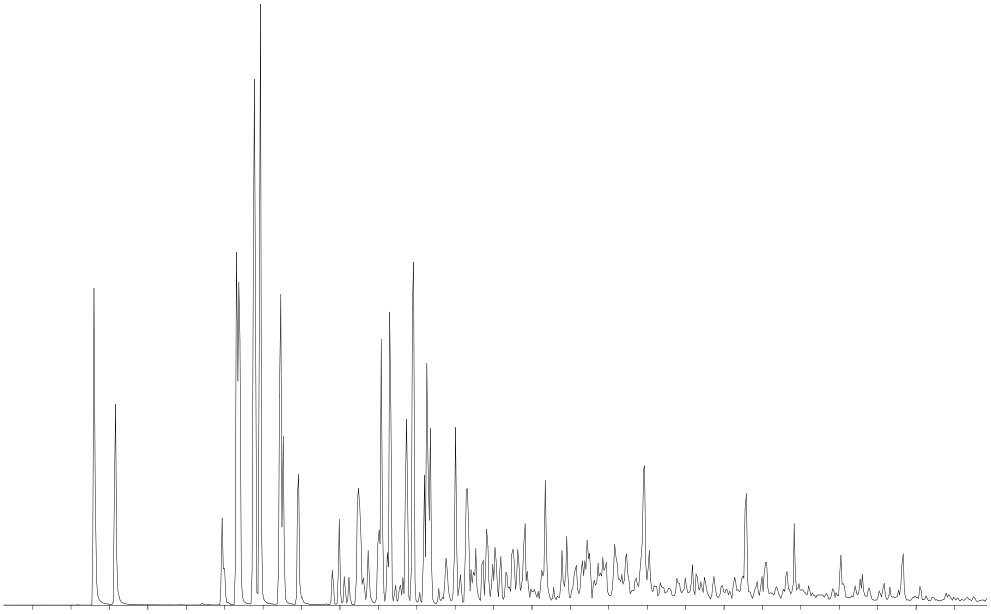
MOR-91 (m/z 142+156+170+184+198+212)



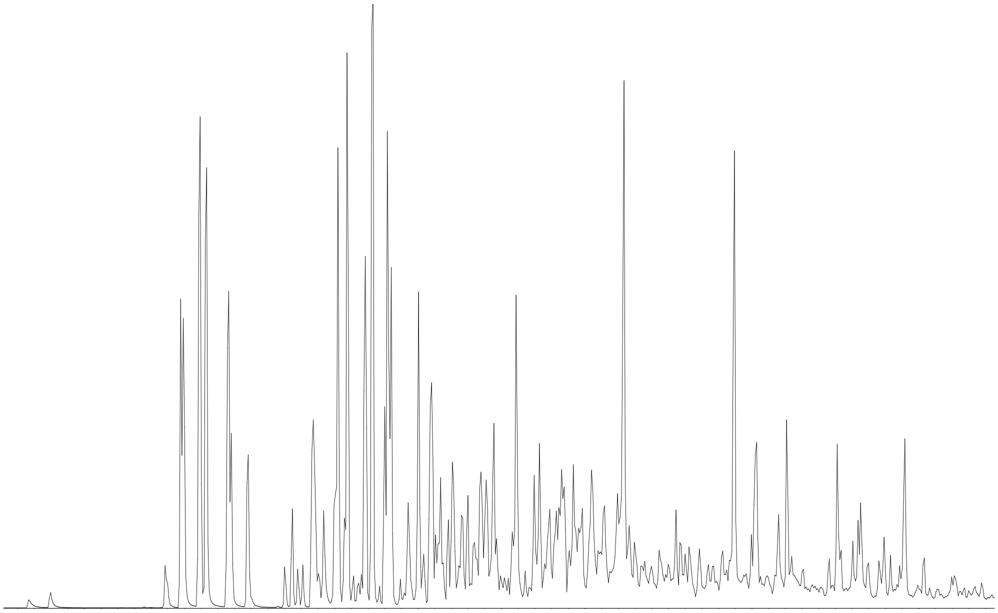
A-1 (m/z 142+156+170+184+198+212)



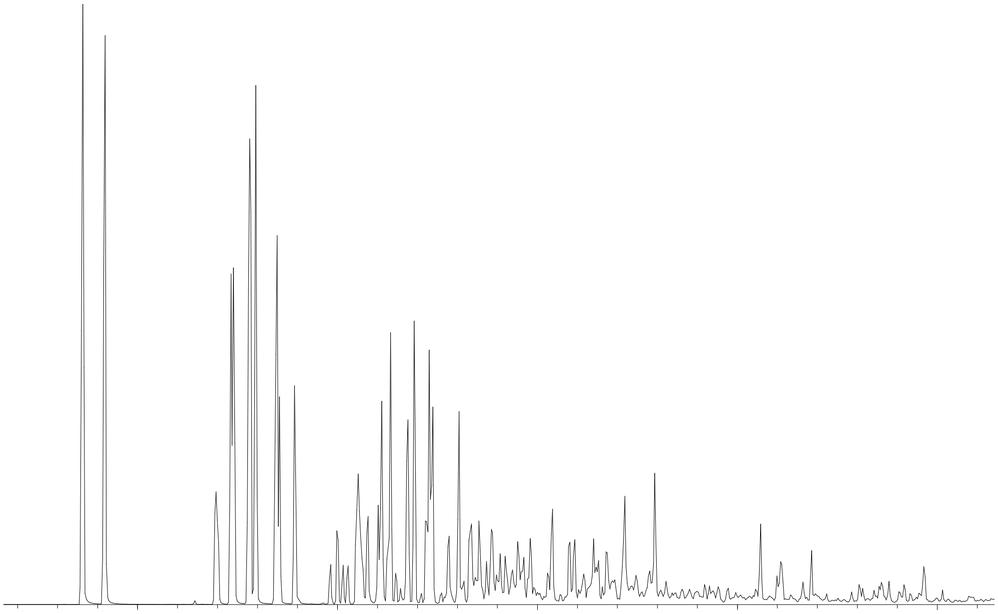
A-20 (m/z 142+156+170+184+198+212)



A-23 (m/z 142+156+170+184+198+212)

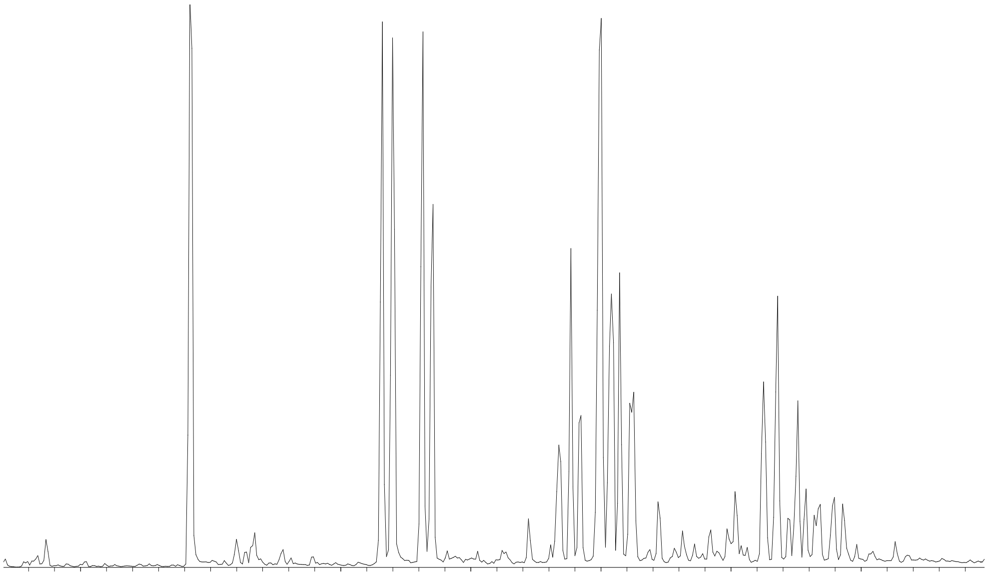


H-3 (m/z 142+156+170+184+198+212)

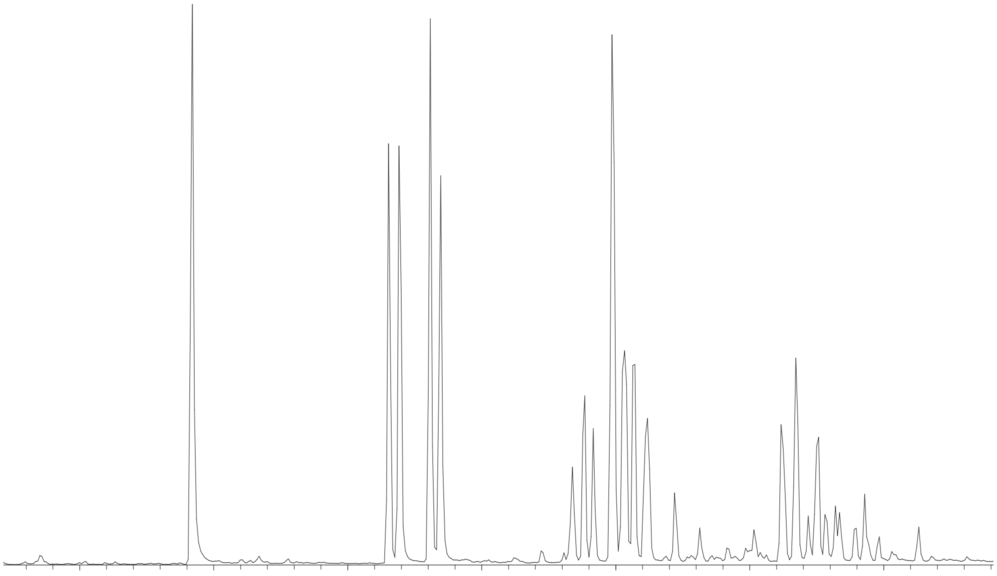


Appendix F: Phenanthrene Distribution of Selected Samples

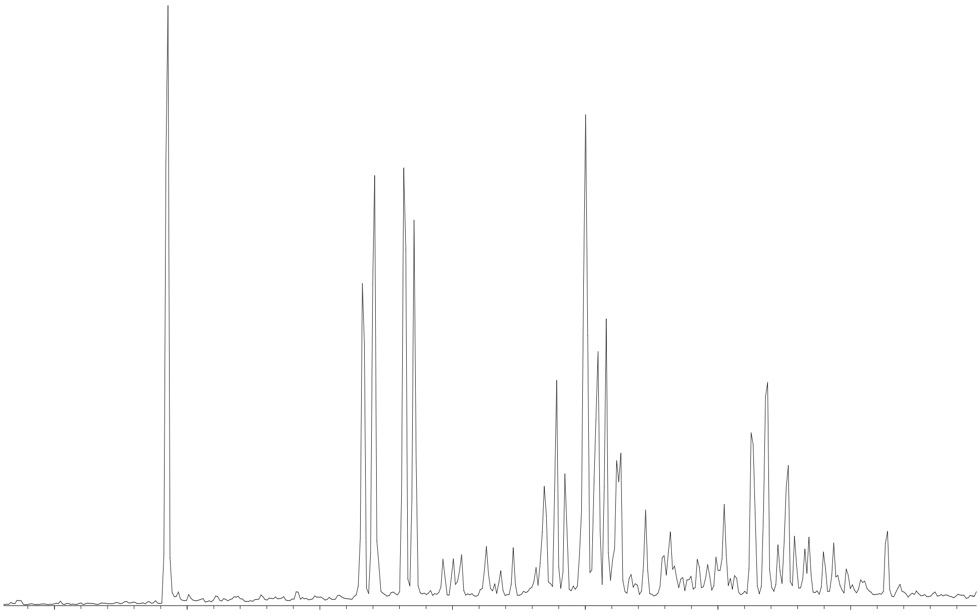
MOR-74 (m/z 178+192+206+220)



MOR-86 (m/z 178+192+206+220)



A-6 (m/z 178+192+206+220)



A-7 (m/z 178+192+206+220)