THE COMPARTMENTALIZATION AND BIOMARKER ANALYSIS OF THE SPIVEY-GRABS-BASIL FIELD, SOUTH-CENTRAL KANSAS

by

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Abstract

The Spivey-Grabs-Basil oil field is a highly developed field in south-central Kansas, having large variability in its production and in the Pineville Tripolite facies. The Pineville Tripolite is the primary producing formation of this field having major isopach variations, possibly influencing production. The hypothesis that the field is highly compartmentalized is from the varied production, isopach and structure of the field. This study investigated the Pineville Tripolite facies in the Spivey-Grabs-Basil Oil Field, with the Basil area the predominant focus, and its possible compartmentalization by looking at the gas chromatograms and their biomarker signatures. This field has had several studies investigating the geophysical attributes, depositional setting and large-scale compartmentalization. Post depositional sea-level changes and possibly syntectonics exposed the Reeds Spring to a sub-aerial environment where meteoric alteration created immense porosity and the Pineville Tripolite facies. Geochemical data shows evidence that this section of the field is sourced from both a marine shale and carbonate source at peak oil maturity, deposited in an anoxic environment. Biodegradation appears very slight, with most alterations transpiring in the alkane ranges only, leaving all other susceptible hydrocarbons unaltered. Compartments within the field are harder to identify when comparing geological data to oil data. Isopach data shows altered thickness of the Pineville Tripolite from well to well, as do Pineville structure values. The isopach and structural data point to possible areas for compartments, but it is from oil geochemical data that compartments become more visible. API gravities and GOR show motley values, but do indicate two significant areas of segregation. The deepest, most southern end of the study showed lighter gravity oils than the middle, suggesting possible fill and spill between the two. However, biomarker abundance indicates three possible compartments. The southern compartment has many more biomarker volumes than do the middle compartment, both divided by a reservoir pinch-out. The third most northeastern well has high biomarker abundance, but shows no geological separators from the other wells. Production from this field may be improved by investigating the biomarkers to allocate these compartments and possible barriers close to wells.

Table of Contents

List of Figures

List of Tables

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Chapter 1 -

1.0 Introduction

Oil fields with varied production rates; formation pressures and reservoir thicknesses have always been a problem plaguing the petroleum industry. This fact is particularly true for the Spivey-Grabs-Basil oil field and this may be attributed to compartments within the field. Like many oil wells drilled in Spivey-Grabs-Basil oil field, wells are drilled with the expectation of producing, but just like several aspects of science, expectations can be proven wrong. These differences occur commonly from the discrepancy in the rocks, subsurface factors and the fluids. Faults, reservoir diagenesis and lithological variations also possess a hand in creating unforeseen compartments leading to the common annoyance of dry wells or unpredicted fortunes. Some major clues can illustrate this common occurrence for some oil fields, those being largely production, reservoir thickness and biomarker analysis.

For many conventional wells the production decline curve tend to decrease in a linear fashion, but there are cases where this is not occurring. For numerous oil wells, production decline curves can show either a severe decline, a nearly flat, or the rare increasing curves. In addition to production slopes, overall performance of wells can be used in evaluating compartment locations. This is indicated when a well is producing fine next to another well of lower production.

Chemical data acquired from the oil, gas and brine of a particular reservoir can be used to ascertain the origin, migration history, accumulation and alteration to these fluids. This data can also provide clues to the relationships between the fluids and reservoir, and also define compartments. For reservoir brines, it is possible for evaporation, filtration, mineral precipitation and dissolution, and the mixing of different waters for induced variations. Oil discrepancies are attributed to source, migration from source, water washing, bio-alteration and age of accumulation. While very similar influences can attribute to gas variations, more commonly biological inputs and source are the main factors when discussing alterations to oil.

The purpose of this study is to present the oil biomarker and geology of the Mississippian Pineville Tripolite facies to assess the compartmentalization in the Spivey-Grabs-Basil oil field, in Kingman county, Kansas (Figure 1).

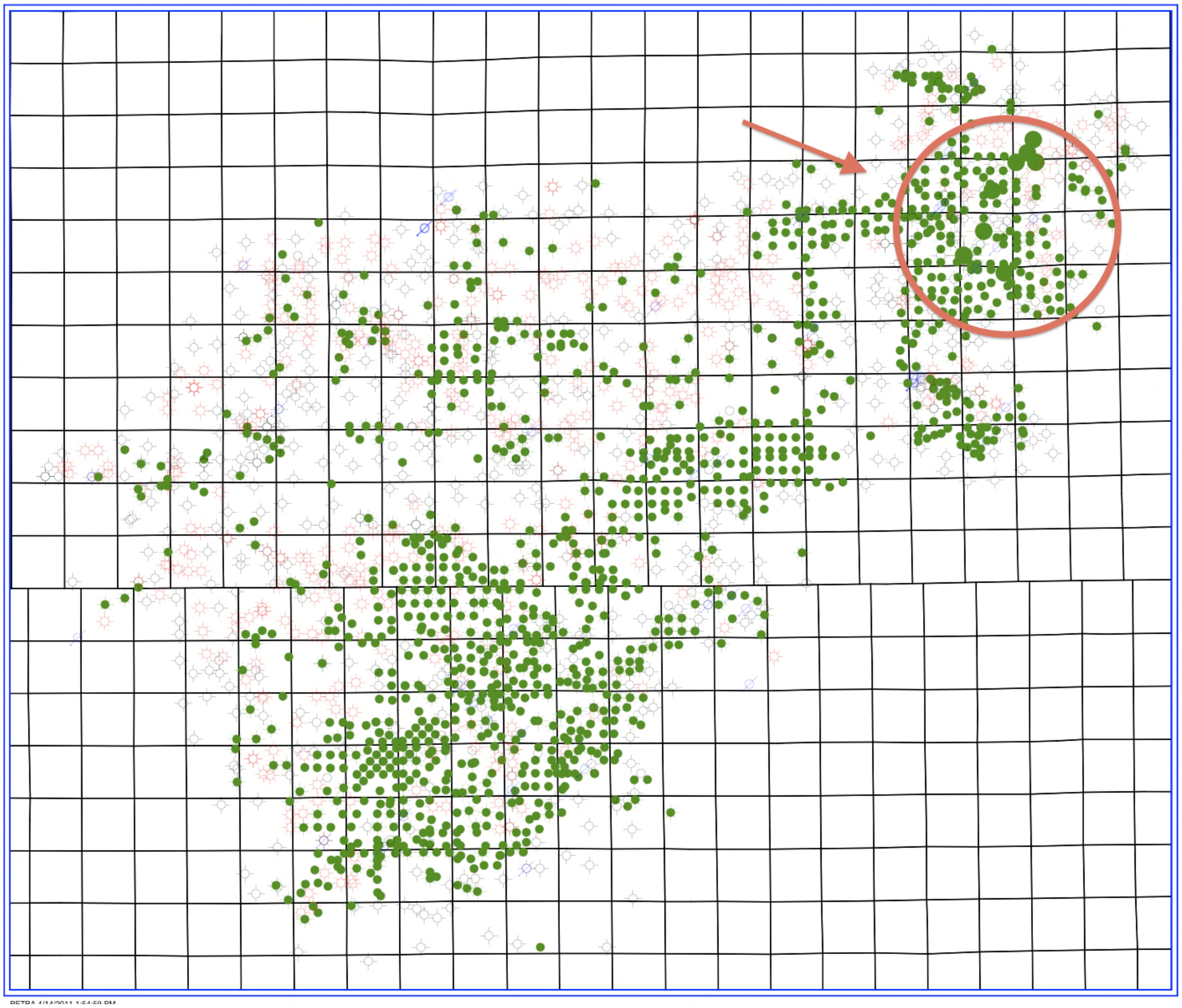


Figure 1. Map of Spivey-Grabs-Basil oil field with study area circled.

1.1 Objectives

In explaining why analyze the Spivey-Grabs-Basil oil field, the initial response is "Because my former employers suggested it." The understanding of the Spivey-Grabs-Basil Oil Field's compartmentalization is slim in volume, but shows good understanding about the creation of the Mississippian tripolite of the field and its equivalents, plus the geophysical attributes of the reservoir rock. Speculation over Spivey-Grabs-Basil's compartmentalization is common among operators and geologists in Kansas, so the perspective of this investigation appears to be merited.

Similar studies have shown the significance of understanding field habits and allocating compartments. The investigation of the Magnus oil field in the North Sea (Barclay et al. 2000) showed compartments in that field, leading to more efficient drilling strategies and truer evaluation of the reserves left to produce. This conclusion is routine for the many papers discussing reservoir compartments, where different approaches are used, but conclude with similar results.

The aim of this study is to use geochemical analysis of the reservoir fluids to provide a concrete answer to the suspicion about the field's compartmentalization. The identification of the possible compartments could lead to better production and prospecting methods for many geologists in Kansas towards this field. This study will also help in examination and development of other fields surrounding the area of study similar to the Spivey-Grabs-Basil oil field by emphasizing the use of the techniques outlined in this paper for application on other fields. In addition, ideas akin to this one may be bolstered from this study, leading to more papers analyzing fields with questionable production and approached with comparable focus.

Furthermore, evaluation of oils from this study could encourage geologists to question where the petroleum of Kansas is sourced. Common assumption is that oil is migrated out of the Anadarko Basin, where temperatures suitable for the creation and expulsion of petroleum from several source rocks (Philp et al. 1997). Philp et al. (1997) analyzed a succession of sedimentary rocks such as Lower Pennsylvanian, Mississippian, Devonian, and Ordovician rocks, all of which are present in Kansas.

1.2 Literature Review

Compartmentalization studies of oil fields are very difficult ideas to investigate. Several papers have shed light upon the subject, the difficulties and the methods commonly used in these investigations. Common practice towards this kind of investigation is the correlation of oil-to-oil, source-to-oil correlation, production history and water compositions. After a thorough literature search on the Spivey-Grabs-Basil Oil field, I concluded that this field was overlooked for compartments by other investigators.

Oil properties are useful in determining source characteristics from oil properties, ascertained from oil biomarkers. Johnson et al (2003) used several parameters when correlating oils to source rock by analyzing geochemical properties of chosen oils and possible source rocks in Mongolia. From that paper, it was proven that the oils of Mongolia were from the same algal source and proved that geochemical parameters are useful in determining source. Biomarker analysis used in that study also indicated application for grouping and separating oils of various locations to like sources. Stevenson et al (2004) wrote a paper investigating the affects that biodegradation had on oils in Northern Montana and Southern Alberta. Their paper unveiled that maturity, alteration and biodegradation of oils can be indicated by several biomarkers and that location of oils relative to source is obtainable from these geochemical parameters.

Correlation and compartmentalization of oils is quite useful when using geochemical properties. This was proven achievable by Milkov's et al (2006) paper where a study into Horn Mountain oil field in the GOM when oil fingerprinting from different oil wells indicated communication, fluid flow and new compartments. Gussow (1954) has a pertinent paper discussing field habits for production and how filling of certain fields is indicated by specific criteria and what information proved the idea. It was also from this paper that gas-to-oil ratios (GOR) was emphasized in allocating spill and fill points, and direction of oil migration. England et al. (1994) pointed out the feasibility of using production history and oil properties can clue geologists in on compartments in the Forty Field. Results from this paper showed that in the Forty field had compartments identified by the GOR values showing direction of the source rock and fluid flow, along with oil properties showing density flip was not occurring between to parts of the field.

With respect to the Mississippian tripolite formation, which is the producing formation in the field of investigation, a handful of papers (McCoy, 1978; Watney, 2001; Mazzullo, 2009; Montgomery et al, 1998; Rogers, 2001) have investigated the origin and characteristics of Mississippian rocks in the mid-continent, unraveling the mystery behind these poorly understood formations. McCoy (1978) discussed exclusively the Spivey-Grabs-Basil oil field and huge compartments in the field and the foundation behind them. He hypothesized valley-infill from in pre-Warsaw dendritic channels sub paralleling lineaments in the field, perhaps indicating Osagean topography. Mazzullo (2009) discussed in great detail the Mississippian strata of south-central Kansas's subsurface, with much emphasis on the Cowley formation. The Cowley formation is a highly productive formation of southern Kansas and northern Oklahoma and could be a stratigraphic equivalent to the Pineville Tripolite facies. Watney (2001), Rogers (2001) and Montgomery et al. (1998) all discuss the Mississippian “Chat,” an equivalent to the Pineville facies, discussing the composition, depositional settings and common characteristics of the formation.

1.3 Geological Setting

The study area is located within the Spivey-Grabs-Basil field in south-central Kansas, in the western most extents of the Sedgwick Basin. The field covers an area greater than 400 square km, where the total acreage is 117,520. The field itself is part of a series or “fairway” of Mississippian oil fields flanking the Central Kansas Uplift structure producing out of very similar formations of Osagean age rocks (Figure 2). Much of Kansas during Osagean time was a carbonate shelf environment deepening from a shelf margin into a basinal environment southward, with changes in sea level occurring commonly (Witzke and Bunker, 1996). This separation and creation of different environments brought about several distinctive types of sediments being deposited: shales, carbonates and cherts; each unique to their own time.

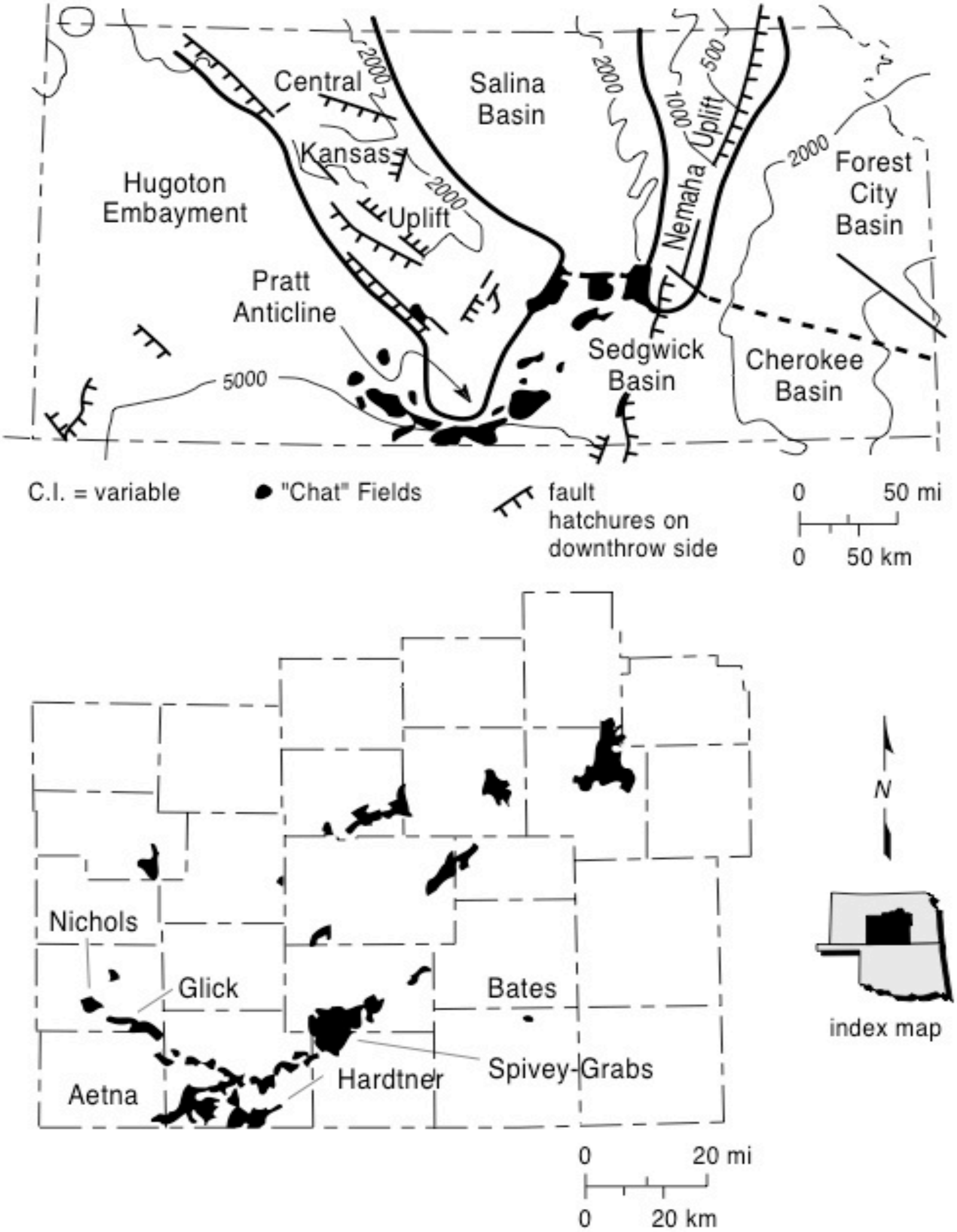
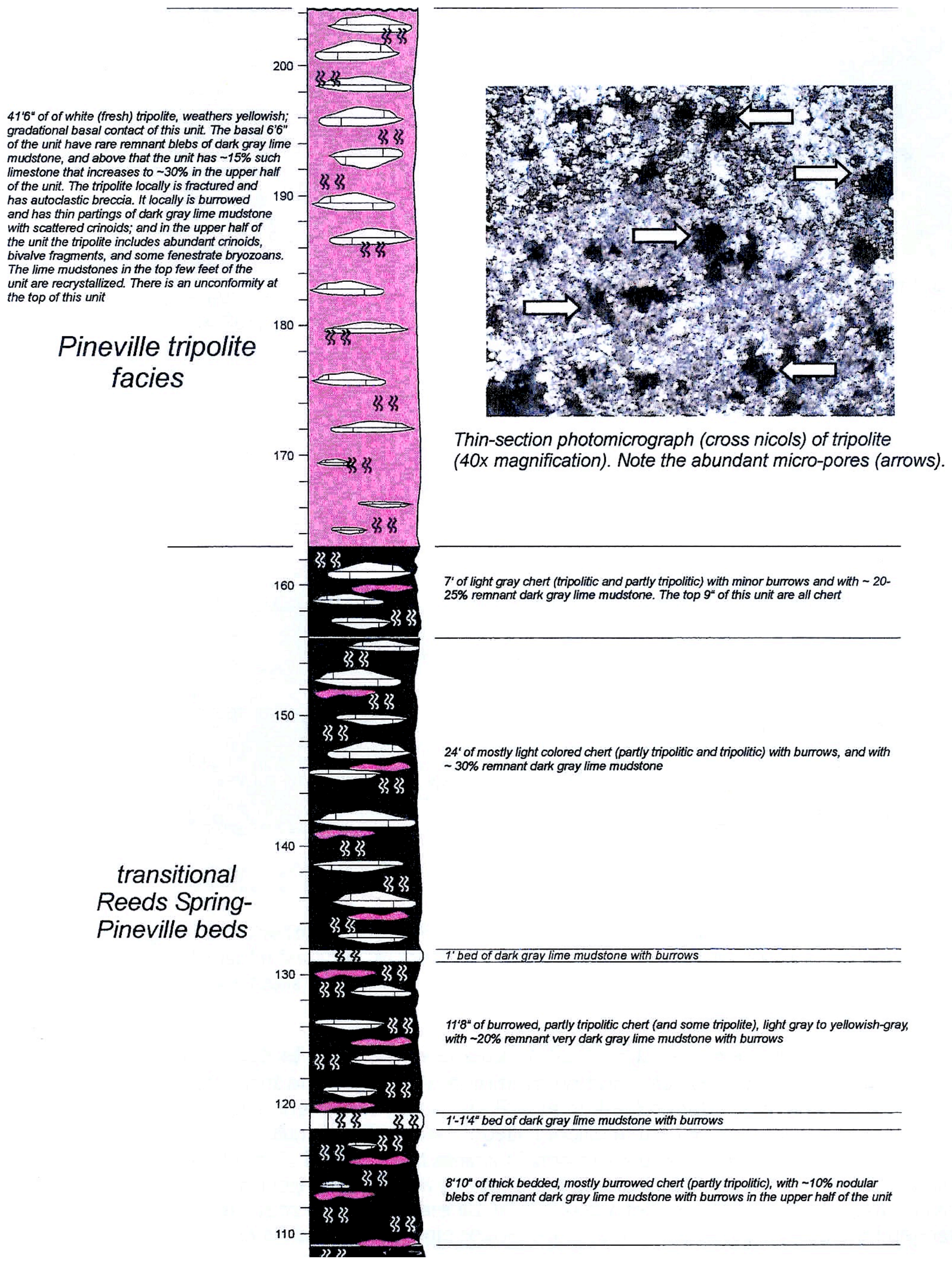


Figure 2. Location of the Spivey-Grabs-Basil oil field in relation to surrounding structures. (Watney et al., 2001)

The Mississippian system rocks are broken down into several stages: Kinderhookian, Osagean, Meramecian and Chesterian, progressing from oldest to youngest. The Osagean stage is underlined by the Kinderhookian stage having the Chattanooga shale, Compton LS and the Northview shale conformably contacting the lower Osagean Pierson formation, another carbonate. The Compton, and Pierson limestones were both deposited on ramp to distally-steepening ramps, where the Northview formation a purely ramp environment (Mazzullo et al. 2010). Overlying the Pierson is the Reed Springs formation, showing profuse amounts of interbedded chert in limestone at outcrops in Missouri (Thompson, 1986) with high amounts of observable organic material. Mazzullo et al. (2010) states that the Reeds Spring was deposited during the deepest water depth of the Kinderhookian to Osagean times on a ramp. A top most part of the Reed Springs lies an highly altered, tripolitic chert, which Mazzullo and White (2010) coined as the "Pineville Tripolite facies" at outcrops of SW Missouri (Figure 3). For consistency, the producing formation of the Spivey-Grabs-Basil field shall be called the Pineville Tripolite facies for the duration of this paper. Overlying the Pineville facies is an unconformity between the Mississippian Osage and Pennsylvanian strata.

The stratigraphy in the field of study is more complex than the surrounding region, having only the Kinderhookian and Osagean stages present from the Mississippian period. The Kinderhookian strata is varied in several areas, creating thickness variations ranging from 100 – 350 ft, where structural changes in the Chattanooga influence the thickness and presence of the Compton and Northview formations. The Osagean stratigraphy is even more complex, as indicated by the highly varied thicknesses of the Reed Spring formation and Pineville tripolite facies. The thickness of the Pineville is influenced greatly by post-depositional influx of meteoric waters, where areas having far more alteration than others creating broadened Pineville tripolite facies ranging from 5 – 70 ft.



41'6" of of white (fresh) tripolite, weathers yellowish; gradational basal contact of this unit. The basal 6'6" of the unit have rare remnant blebs of dark gray lime mudstone, and above that the unit has ~15% such limestone that increases to ~30% in the upper half of the unit. The tripolite locally is fractured and has autoclastic breccia. It locally is burrowed and has thin partings of dark gray lime mudstone with scattered crinoids; and in the upper half of the unit the tripolite includes abundant crinoids, bivalve fragments, and some fenestrate bryozoans. The lime mudstones in the top few feet of the unit are recrystallized. There is an unconformity at the top of this unit

Thin-section photomicrograph (cross nicols) of tripolite (40x magnification). Note the abundant micro-pores (arrows).

7' of light gray chert (tripolitic and partly tripolitic) with minor burrows and with ~ 20-25% remnant dark gray lime mudstone. The top 9" of this unit are all chert

24' of mostly light colored chert (partly tripolitic and tripolitic) with burrows, and with ~ 30% remnant dark gray lime mudstone

1' bed of dark gray lime mudstone with burrows

11'8" of burrowed, partly tripolitic chert (and some tripolite), light gray to yellowish-gray, with ~20% remnant very dark gray lime mudstone with burrows

1'-1'4" bed of dark gray lime mudstone with burrows

8'10" of thick bedded, mostly burrowed chert (partly tripolitic), with ~10% nodular blebs of remnant dark gray lime mudstone with burrows in the upper half of the unit

Figure 3. Stratigraphic column of the Reeds Spring and Pineville Tripolite. (Mazzullo et al., 2010)

The structure of the field is quite simple from a broad point-of-view, but complex upon closer examination. The Pineville tripolite top increases from structural low in the southern part of the field increasing higher towards the north in gradual incline creating a structural trap. The structure of the overlying stratigraphic sections mimics the Pineville tripolite's structure, with a few minor changes, but nothing too significant. However, the structure of the Pineville tripolite base is quite varied throughout the field. This leads to varied isopach maps and to the varied locations for production do to pinch outs making the field to having stratigraphic traps. This variation is quite prevalent between wells spaced 200m apart (Watney, 2001) and maybe from pre-Warsaw dendritic events (McCoy, 1978) eroding away the very porous Pineville. Mazzullo et al. (2011) attributes similar thickness features in Missouri to syn and post depositional tectonics.

The northern extent of field is abrupt and definitive, as discussed by Watney (2001), who described the Pineville tripolite base as uplifted 55 m, pinching the formation out. The southern and surrounding boundaries of the field is defined by the transition of the porous Pineville tripolite into a cherty dolomite, suggestion the limit of meteoric alteration and movement into a more basinal depositional area. Watney et al. (2001) noted that while the lithology changes from the tripolite to dense interbedded dolomite, the overall thickness of the equivalent formations is maintained.

Initially the Spivey-Grabs-Basil oil field began oil production out of the Pineville Tripolite facies in 1949 in T31S R9W Sect. 13 at a depth of 4,398 feet. Continued exploration in the Pineville facies found that gas is also present further increasing prospective drilling. That increase in drilling found successive discoveries in Lansing-Kansas City, Viola, Cherokee, Permian and Simpson formations and has added to the production volume, but has only accounted for a small percent of the field's total production values which is still dominated by Pineville production. As of now, cumulative production has reached 68,905,758 barrels of oil with gas volumes reaching 837,807,811 thousand cubic feet from 811 oil wells and 721 gas wells. Despite of an average decline rate of 14% throughout the field, several companies are still developing the field.

1.4 Study Area

The Spivey-Grabs-Basil oil field has an area measuring 380 square km with thousands of well drilled. The shear size and number of well lead the need for a smaller study area within the field for many other reasons such as time, money and educational objectives. Another principal factor was the need for a freshly drilled and fractured oil well, which became the Maple 2F oil well narrowing the scope to T29S-R7W Sec 24, 25, 26, 35, 36; T30S-R7W Sec 2 (Figure 4 and Table 1). This area was capable of providing a small and concise idea of what is generally occurring in the overall field. Within the area, there were 107 wells drilled, but only 33 wells are producing in the area. This amount of well control and information is helpful, but the lack of wells producing and the limited amount of permission for well fluid acquisition has hampered certain aspects of the study.

The Spivey-Grabs-Basil field was chosen as the study area for several reasons: 1) that bulk production comes from the Mississippian Tripolite; 2) known heterogeneity in its production; 3) large volumes of petroleum produced; 4) for being highly developed; 5) newly drilled well and 6) for ease of access.

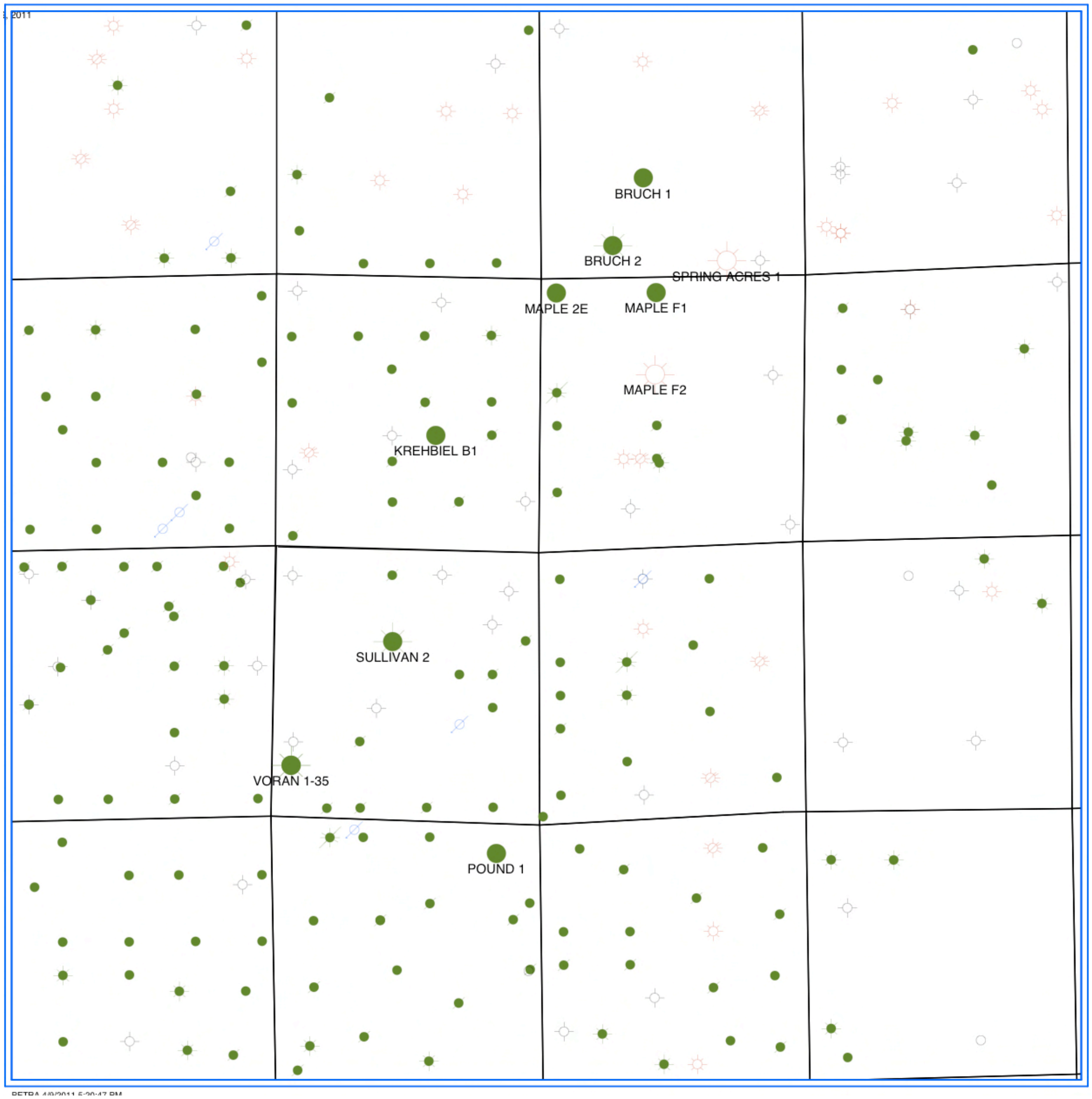


Figure 4. Map of study area showing well locations and well names analyzed.

Well Name	Township and Range	Spot Call	Producing	Producing Interval	Sample	Production Designation
Pound 1	T30S R7W	Sec. 2, C W2 NE NE	Pineville	4130-4140	Oil	Oil
Bruch 1	T29S R7W	Sec. 24, C NE SW	Pineville	4202-4210	Oil	Oil
Spring Acres 1	T29S R7W	Sec. 24, SE SW SE	Pineville	4122-4130	Oil	Gas
Maple E2	T29S R7W	Sec. 25, NW NW NW	Pineville	4140-4200	Oil	Oil
Maple F1	T29S R7W	Sec. 25, C NE NE NW	Pineville	4140-4150	Oil	Oil
Maple F2-3rd hour	T29S R7W	Sec. 25, SW NE NE SW	Pineville	4127-4137	Oil	Gas
Sullivan 2	T29S R7W	Sec 35, NE SE NW	Pineville	4120-4128 4147-4154	Oil	Oil and Gas
Krehbiel B1	T29S R7W	Sec 26, NW NW SE	Pineville	4162-4172	Oil	Oil
Voran 1-35	T29S R7W	Sec. 35, NW NW SW	Pineville	4124-4134 4147-4149	Oil	Gas
Maple F2-4th hour	T29S R7W	Sec. 25, SW NE SE SW	Pineville	4127-4137	Oil	Gas
Bruch 2	T29S R7W	Sec. 24, S2 SW	Pineville	4132-4142	Oil	Oil and Gas

Table 1. Well names, locations and other important characteristics.

1.5 Production Data and Field History

The Spivey-Grabs-Basil field was discovered in the 1950s with production development expanding vigorously because of the large volumes of oil and gas being produced out of many oil wells. Production primarily is out of the Osagean stage tripolitic chert within lower Mississippian period. The tripolitic chert is directly at an unconformity with overlying Pennsylvanian Period stratigraphy called the Cherokee formation. Mazzullo et al (2009) suggested that this formation is more appropriately called the Pineville Tripolite facies of the Reed Springs Formation, rather than just giving it an arbitrary Osage stage designation. The tripolitic chert is created where in-situ chert has been altered by the influx of meteoric water, which coincides well with the unconformity overlying the Mississippian stratigraphy in this field.

1.6 Compartmentalization

The evaluation and identification of compartments in an oil field is a key objective in developing an oil and gas field. Several data sets are used when determining a field's possible compartments: cores, well cuttings, well logs, seismic, pressures and geochemical data (Badgett et al., 1996; Edman and Burke, 1999). According to Milkov et al. (2007) several parameters that indicate the presence of flow barriers and compartments are:

1. Lack of lithological homogeneity from cores and well logs
2. Discontinuity seismic reflectors
3. Pressure disequilibrium
4. Uncommon oil-water contact
5. Dissimilar geochemical properties

Because of the limitations and availability of certain parameters toward this study, the use of well logs, and oil biomarker analysis will be used to identify compartments.

Chapter 2-

Stratigraphy and Deposition

2.0 Stratigraphy

When discussing the stratigraphy and deposition of a sedimentary rock layer, special attention should be given to that rock's origin, form, and the relationships with its spatial and temporal surroundings. The Spivey-Grabs-Basil oil field is located along the Kingman-Harper county border in south-central Kansas, producing out of the Pineville Tripolite facies (Mazzullo et al. 2011), which is deemed the top most unit of the chert-rich Reeds Spring formation by Mazzullo et al. (2011) being the highly altered chert section. The Pineville and Reeds Spring are both members of Osagean series rock in Mississippian age (Figure 5). The Mississippian Period is itself comprised of the lowest Kinderhookian series, followed by the Osagean, Meramecian and the shallowest Chesterian series contacting Pennsylvanian Period rocks. According to Maples (1994), the Osagean series contains the following formations: the Pierson, Reed Springs, Elsey, Burlington-Keokuk and lower parts of the Warsaw formation.

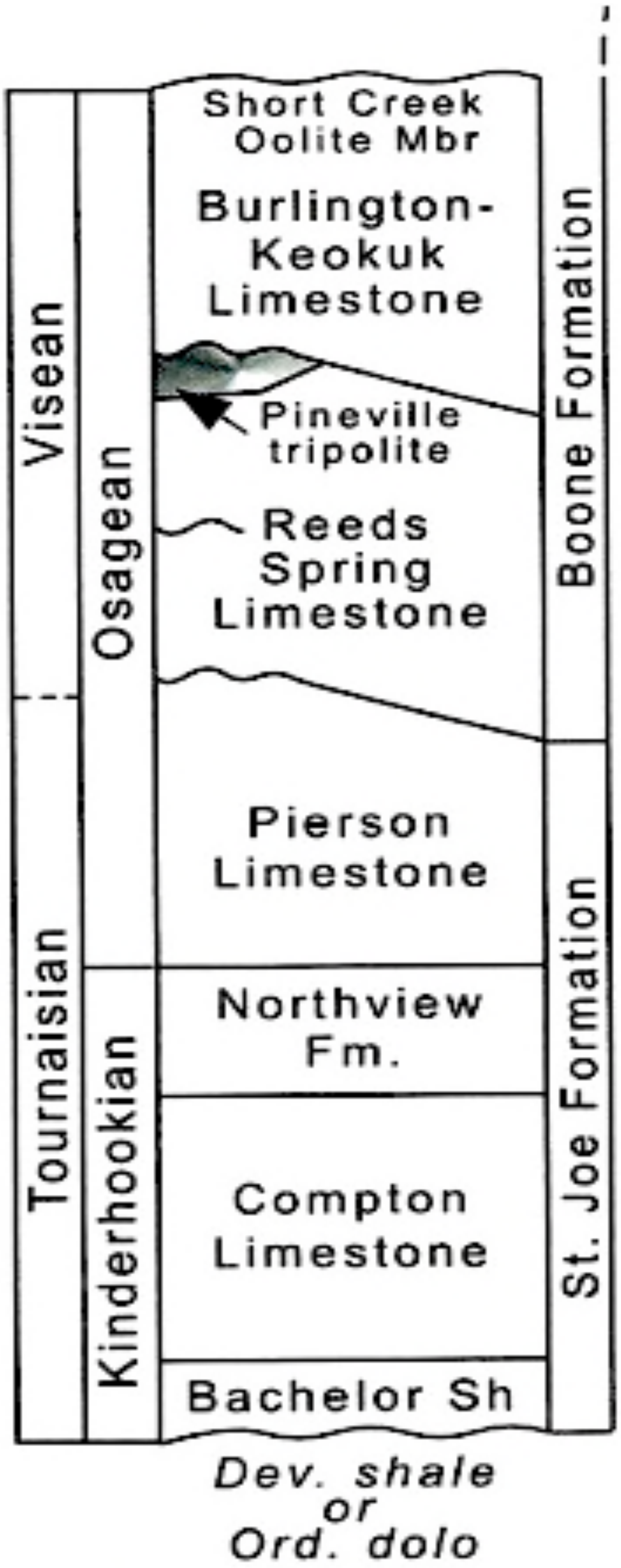


Figure 5. Generalized stratigraphic column of Osagean Stage. (Mazzullo et al., 2011)

Unconformably underlying the Reeds Springs/Pineville Tripolite is the Pierson formation. The Pierson is a dolomitic limestone having thicknesses of 10 feet to around one hundred with several cross-bedded limestones, structures and crinoid fossils. Several outcrops of this formation in Missouri show evidence of transgressive-regressive cycles just in this single formation as noted by Mazzullo et al. (2010) when he observed crinoid sands that coarsen upwards indicating regression, green shale cap in locations and unconformable contact with the Burlington-Keokuk formation. In the study area it was observed that this formation has chert nodules located in-situ, but sparsely, in well cuttings. Petrophysical logs made picking this formation out easy because of the rocks tight appearance from porosity and resistivity logs, plus the clean appearance on the gamma ray track.

Directly above the Pineville Tripolite facies is the Cherokee Group of the Des Moinesian Series from Pennsylvanian age. This contact is a definitive unconformity, where the Burlington-Keokuk formation, Meramecian and Chesterian series of Mississippian age are missing, along with Morrowan and Atokan series of Pennsylvanian age. The Cherokee group has many members and lihologies such as shales, sands, and coals brought about by many sea level changes. The coal members are associated with very shallow seas, shale members came about from lowland inundation and deep seas. The sand members are commonly in bar or stringers form from regressive seas. Howe (1956) noted that in southeastern Kansas, the Cherokee Group reached thicknesses of 450 to 500 feet. Basinal areas were favorites for this group as shown by thick Cherokee strata in the Cherokee Basin, Anadarko Basin and the Hugoton Embayment (Merriam, 1963).

At outcrops in Missouri, the Reed Springs formation is noticeably dominated by inter-bedded nodular, black, cherty lime mudstones that has a substantial thickness (200 feet) where the inter-bedded chert near the top part of the formation bearing tripolitic alteration and is heavily fractured and burrowed. The Pineville Tripolite is wedged between the Reed Springs formation and the overlying Burlington-Keokuk formation. The Pineville Tripolite facies is a highly altered chert facies of the Mississippian system, located in the Mid-continent region of the United States (Mazzullo, 2010; Montgomery, 1998; Parham and Northcutt, 1993; Rogers, 2001; Watney, 2001). The facies is located in Kansas, flanking the Central Kansas Uplift and the

Nemaha Uplift structures (Montgomery, 1998) forming an informal “chat fairway” term describing the overall location of Spivey-Grabs-Basil Oil Field and others like it.

2.1 Deposition

During Osagean time, Kansas was part of a larger carbonate shelf of the mid-continent (Watney et al., 2001,) containing an inner and main shelf, and a shelf margin. At this time, Kansas was positioned close to the pre-historic equator, around 20° south latitude (Witzke, 1990) having dry conditions, perfect for carbonate precipitation. However, the setting of the study area during this time was on a shelf margin, allowing for the deposition of the chert-rich Reeds Spring formation (Mazzullo et al., 2011) during a highstand system tract on a more ramp-like environment. Watney (2001) and Rogers (2001) both hypothesized the chert-rich formation precipitated out of solution from silica-saturated waters, possibly from volcanism. A finding by Lane and De Keyser (1990) was that during Osagean time, much of Kansas was a carbonate shelf, and shelf margin deepening into the clastic Anadarko basin to the south. . Witzke and Bunker (1996) and Al-tawil et al. (1999) also discovered that during Osagean time, correlative rocks of Iowa and Tennessee show T-R cycles. Watney et al. (2001) discussed that the subsurface rocks in Kansas showed similar T-R cycles within cores from Spivey-Grabs-Basil oil field.

Creation of the Pineville Tripolite facies in the Reeds Spring formation likely occurred because of major sea-level changes and tectonics. Mazzullo et al. (2011) stated that this occurred following a major eustatic low-stand system track, and uplifting. Exposure from these events allowed the Reeds Spring to be highly altered by meteoric waters, creating the highly porous, low permeability reservoir rock in the Spivey-Grabs-Basil Oil field (Figure 6). It is also because of these events, in collaboration with tectonics, that the Pineville Tripolite facies lies unconformably below the Pennsylvanian Cherokee Formation.

In south-central Kansas it is observed in logs and well cuttings that the Chesterian and Meramecian are absent, leaving the Osagean Series in direct contact with Pennsylvanian Period age rocks creating an unconformity. In addition to this unconformity, Watney et al (1999) observed magnetic lineaments with in the pre-Cambrian bedrock trending northeasterly, suggesting movement in the basement rock. Northwest of the field running parallel with this lineament is an area of major significance. There is thickening between the upper Devonian and lower Mississippian age rocks with clastic sediment. There is also a thickening of Mississippian age carbonate rocks southeast of the field. It is also observed that between the Central Kansas Uplift and the Nemaha Uplift that the Mississippian thickness of tripolitic rocks increase dramatically overlying the clastic sediment dump during late Devonian time. Watney (1999) suggests that this occurred due to reactivation of the area of the basement movement during Devonian and Mississippian time.

The unconformity between the Mississippian-Pennsylvanian rocks may have been another leading factor for the alteration of the Pineville tripolite. From continued tectonic activity eroding away the shallower formation, fresh meteoric water was introduced to the exposed surface allowing for the Reeds Spring formation to alter. These tectonic influences may have occurred from the Ouachita Orogeny hundreds of miles southeast in Arkansas, and from the nearby Central Kansas Uplift and Nemaha Uplift. All of these structural events occurred during middle Mississippian to late-Pennsylvanian times (Keller and Cebull, 1973; Thomas, 1985, 1989). More evidence of tectonic activity occurring in the study area (Figure 8) is from the highly varied isopach thicknesses of the Pineville Tripolite and high structural alteration of the Pineville Tripolite (Figures7 & 8).

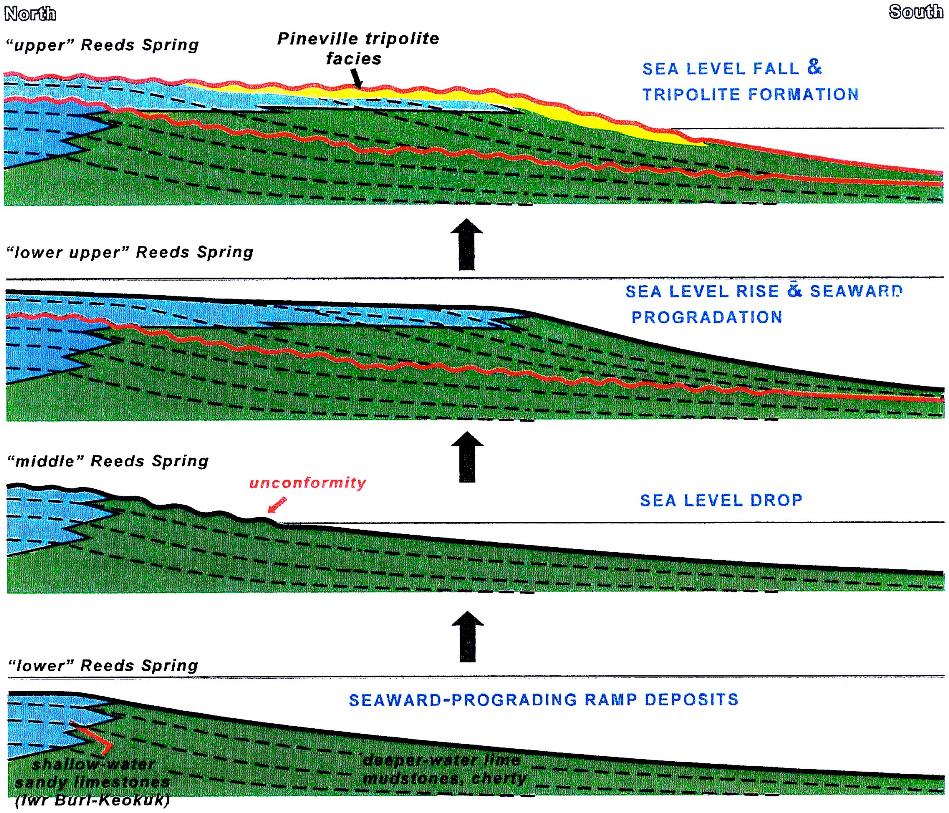


Figure 6. Depositional example of the Reeds Spring Formation and Pineville Tripolite facies. (from Mazzullo et al., 2011)

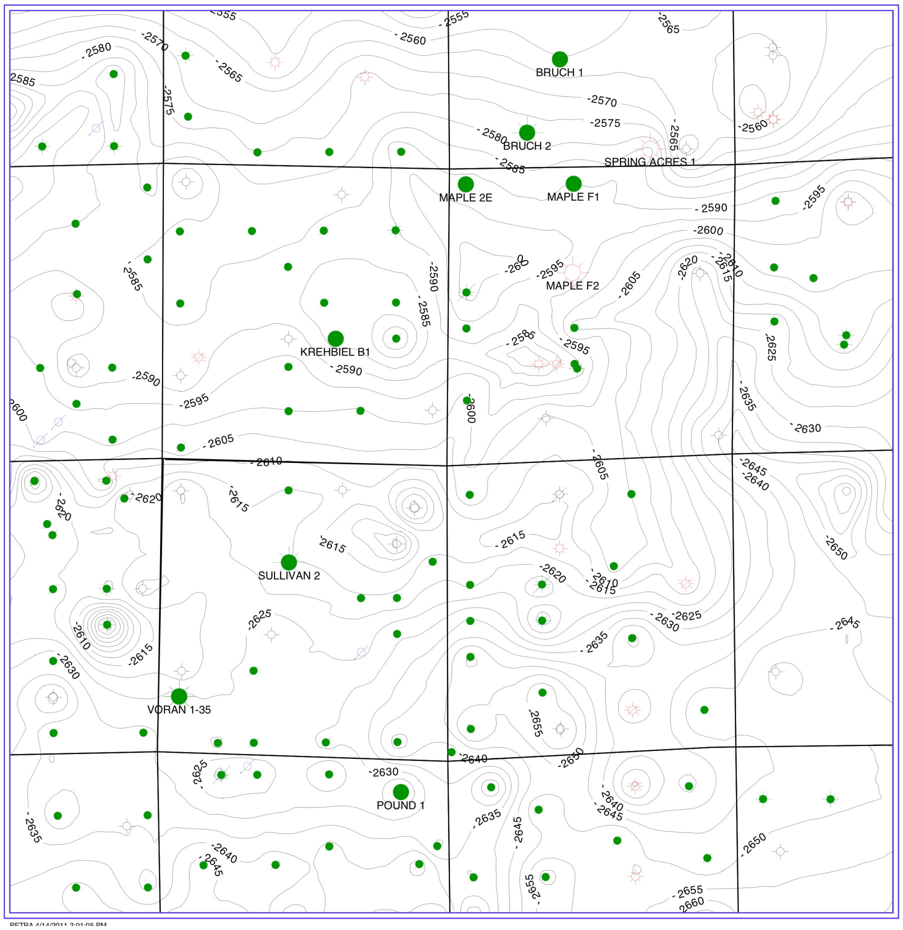


Figure 7. Structural map of the Pineville Tripolite facies.

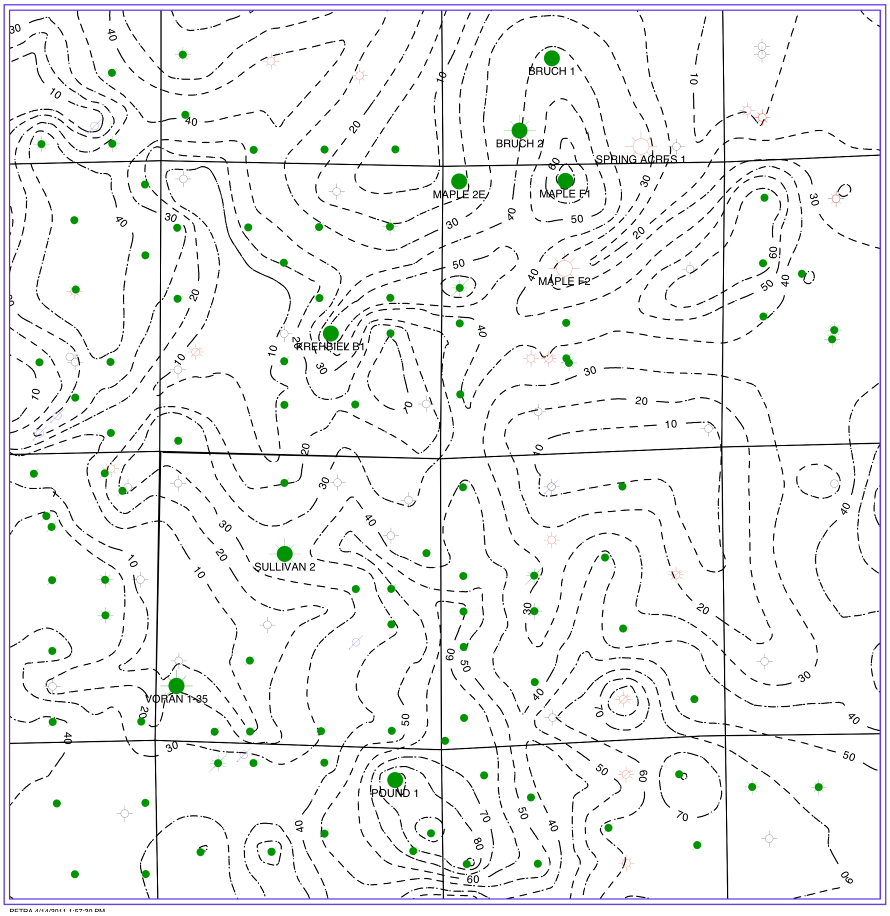


Figure 8. Isopach map of the Pineville Tripolite facies.

Chapter 3 –

Oil Biomarkers

3.0 Biomarkers

Biomarkers are gaining ground in their application in the petroleum industry and have a history of achievements. Understanding biomarkers was one of the first ideas cementing their use among scientists. Biomarkers are very complicated, but can be clearly defined as molecular fossils (Eglinton et al., 1964) putting them in area of former living organisms such as eukaryotes, and prokaryotes. Biomarkers are highly complex organic compounds of hydrogen, carbon and other elements occurring in soils, rocks and crude oils. Even when millions of years have passed, these molecules show little, if any, alteration from their parent living organism (Moldowan et al, 2005). Because of this trait, these complex organic structures can reveal many characteristics about their origin, unlike other compounds.

Several characteristics of biomarkers in oils are very useful such as evaluation of the type of source, the maturity of the oils and alterations incurred upon the oils following accumulation. The three types of biomarker groups most useful in identifying these parameters are steranes (m/z 217), terpanes (m/z 191) and n-alkanes. Other biomarker groups are also useful in identifying other more specific traits of oils, which include: n-alkylcyclohexanes, isoprenoids and steroids (Moldowan et al. 2003).

3.1 Steranes

Steranes are becoming continued identifiers in geochemical analysis of oils and source rocks in petroleum exploration. Steranes (m/z 217) are important to understand because of this application towards petroleum. Volkman (1988) found that eukaryotic organisms are the leading sources for steranes whose presence comes about from alteration of sterols. Sterols are a series of three-6 carbon rings (A,B, C rings) and one-5 carbon ring (D-ring) with a -OH-group bonded to the 17th carbon atom of the D-ring (Figure 9). Instead of an –OH bonded to the 17th carbon, a chain of alkanes will bond, creating our sterane, see figure 10 (Waples, 1990). Commonly, steranes have 27 through 30 carbons in the total base sterane structure, where other sterane chains can be derived from various stereochemistry (α, β and R, S) to specific carbons and carbon chain lengths.

The defining difference between regular and stereochemically altered steranes are the placements of the hydrocarbon chains on the 5, 14 and 17 carbon atoms on whether they are towards or away the structural axis. If the chains are below the plane it is referred to as alpha (α) and above is beta (β). This is an important factor because as a source matures, the more β bonds are created versus α-bonds (Seifert and Moldowan, 1986), meaning the β-bond is more structurally sound than the α-bond. However, Ten Haven et al. (1986) showed that the β-bonded steranes could be produced in sulfur-rich environment prior to the maturity normally required. Another isomer for sterane is the 20S and 20R isomers, and these are indicators of source rocks maturity, because of the source of the two. The less thermally stable 20R isomer comes from strictly biological inputs in young sources, which is converted to 20S isomer, as found by Mackenzie et al. (1983). Over time, this ratio will increase to a peak amount of 0.55, where the level should be maintained unless biodegradation occurs.

The most common types of steranes are the "regular" steranes, stereochemically alter to become rearranged diasteranes, which evidence shows are created during catagenesis, but also are source dependent. It is found that shales have higher concentrations of diasteranes when compared to carbonate sources, making this value somewhat misleading. The source dependency of certain steranes is discussed in section 3.4.1.

3.2 Terpanes

Terpanes are another form of organic compounds used as biomarkers for indentify oils, sources and other environmental influences on petroleum. Terpanes are very similar in structure to steranes, but have more variations of cyclic ring structures (3, 4, 5) in the overall compound, but lesser weight and being measured on the m/z 191-gas chromatogram (Figure 10). Terpanes are believed to derive from terpenoid structures of bacteria (Waples, 1990) and do have preference for certain structures at different times of catagenesis and diagenesis. The overall architecture of the terpane structure is resistant to many changes, where the alterations are only incurred upon the number of bound cyclic rings, broken down into three main groups: pentacyclic, tricyclic (figure 10) and tetracyclic.

The most common group is the pentacyclics, having five- carbon rings and 27 to 35 carbons, which is divided into two more groups called hopanoids and nonhopanoids. Hopanoids or hopanes, which they are more commonly referred to as, are the most likely pentacyclic terpane to have highly definable structure influenced by alteration. When this compound is originated from biological inputs, a n-alkyl group is attached to the C-22, but is asymmetrically on the right-side or R giving it the C-22R appearance (Figure 11). Through diagenesis and increased maturity, this alkyl is rotated to the left side of the C-22, making this newer compound the geological form, which is a chief identifier in oils, see figure 11. Hopane (17α, 21β(H)) values can also come from the thermal conversion of moretane (17β, 21α(H)). Source influence of the hopane compound also leads to various compound outputs. Most common of all is the C_{30} 17α-norhopane, or C_{29}. From anoxic carbonates, this compound is prevalent when compared to suboxic deposition environments and to shales. This anoxic environment plays a key influence on other hopanes: C_{34} and C_{35} homohopanes. This kind of environment allows for the preservation of these compounds, prominent of carbonates, too.

Tricyclic terpanes are quite complicated biomarkers having carbon atom numbers ranging from 21 to 35. Waples et al. (1990) states that they believe these compounds, along with tetracyclic terpanes, come from bacteria, but Ourisson et al (1982) suggests that these come from prokaryotic organisms. Tricyclic terpanes have been used in the past by Seifert et al. (1980), Seifert and Moldowan (1981), Zumberge (1978), Peters and Moldowan (1993) to correlated crude oils with source, to predict source characteristics and to evaluate the degree of thermal maturation and biodegradation, which will be discussed in chapter sections 3.4.1 and 3.4.2.

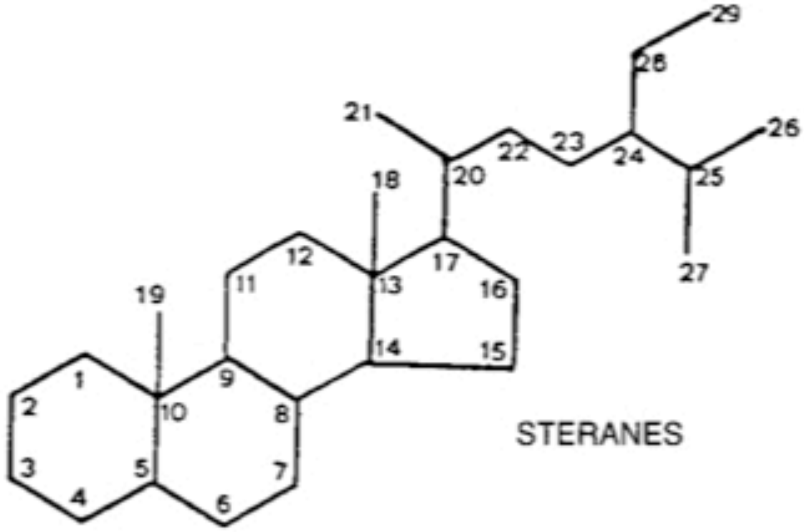


Figure 9. Sterane compound structures. (Waples et al., 1990)

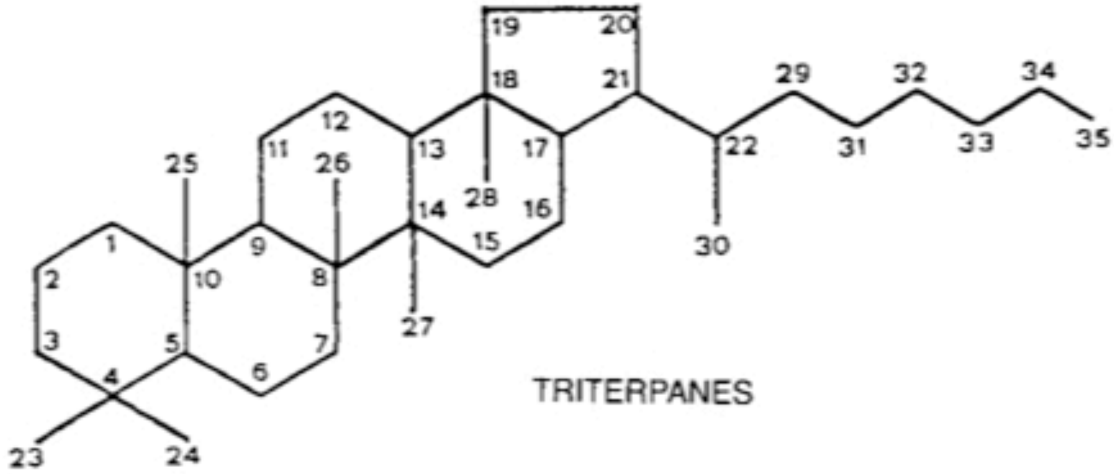


Figure 10. Terpane compound structure. (Waples et al., 1990)

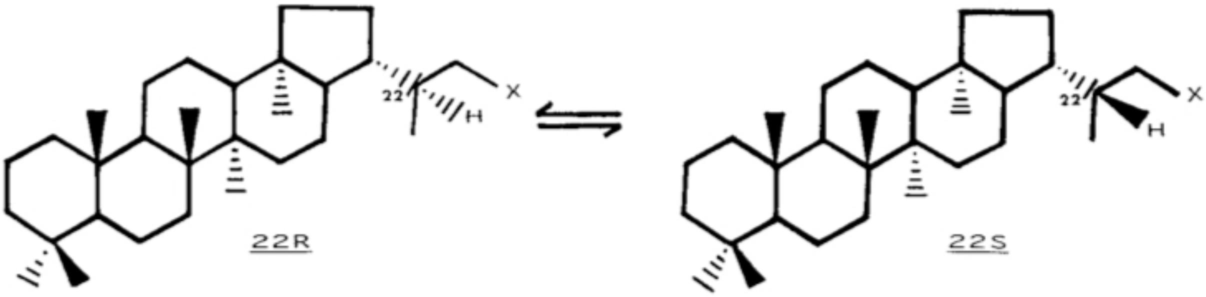


Figure 11. Homohopane epimers of hopane. Highlighting the biological (left) and geological (right) isomers. (Waples et al., 1990)

3.3 n-Alkanes and Isoprenoids

Petroleum hydrocarbon chains run the gamut from alkanes to saturated cyclical hydrocarbons, making analysis somewhat difficult. A more useful and easier series to understand are the normal (n) alkanes and the isoprenoids. These couple of organic carbons can say a lot of information about oil and its story. Alkanes are the combination of carbons and a number of hydrogen atoms needed to satisfy carbon's valence charge of 4. This commonly gives rise to a chemical compound having C_nH_{2n+2}. The number of carbon atoms can greatly increase, reaching even C_{40} amounts, indicating alkane complexity. The most useful n-alkane range used in oil biomarker evaluation is the C_{11}-C_{25}, with special emphasis on the C_{18} and C_{19}, plus the carbon preference index between C_{11}-C_{22} biomarkers.

Isoprenes have a series of five-carbons, and are commonly found in all oil biomarkers and are commonly analyzed using the m/z 57 and the TIC chromatogram. These complex hydrocarbons come about from biosynthesis by polymerizing the appropriate 5-carbons isoprenes (Peters et al., 2005). The two commonly used isoprenoids used in biomarker analysis are pristane and phytane. Both fall into the acyclic, diterpane series where pristane is created by the degradation of phytane by losing a methyl group. In conjunction with n-C_{17-18} chains, much can be interpreted about the source rock and the post-accumulation alterations of an oil.

3.4 Oil Source Rock Evaluations

Fossils on the molecular level are called biological markers or biomarkers as stated by Eglinton (1964), originating from formerly living organisms. These biomarkers also maintain key characteristics from their parent organism such as structure and composition prominent in petroleum and its generation. From oil biomarkers, one can establish several themes concerning a source rock: the type of depositional environment of the source, the lithology of the source, and the maturity of the source. It should be known that the use of biomarkers to determine a source and its depositional environment could only be reliable in oils not severely biodegraded.

For a source rock to become viable for petroleum expulsion and production, the rock must be deposited and altered under the correct conditions. The best depositional environment for a source rock is one with anoxia for organic matter preservation, low energy marine or lacustrine waters and with a plethora of organic matter. In addition to the correct depositional environment, a source rock must undergo several post-depositional alterations in the following orderly for petroleum generation: diagenesis, catagenesis, and metagenesis. Catagenesis, according to Moldowan et al (1993) is the process by which organic matter in rocks is thermally altered by burial and heating at temperatures in the range of ~50-150 degrees Celsius under typical burial conditions requiring millions of years. Moldowan (1993) also defined metagenesis as the thermal destruction of organic molecules by cracking to gas, which occurs after catagenesis at ~150-200 degrees Celsius. The other alteration that must take place is diagenesis, which Blatt (1992) defines as the entire chemical, physical, and biological changes in the characteristics of a sediment accumulation from the time the grains are deposited until they are metamorphosed or melted, excluding weathering.

In the order previously listed, as the source matures the first product is oil, secondly oil and gas, and finally gas. Initial oils produced from a young source rock usually low in gravity (28-36), but increase to the lighter-end gravities when approaching greater maturity as stated by Barker, et al (1988). As progression through the source rock alteration continues, wet gas followed by dry-gas are produced until ultimately the rock becomes inert and no longer produces. Knowing this, it should be stated again that this field of study does produce oil and gas, with the oil gravities ranging from 30-39 API indicating a mature source rock under Barker's criteria.

The three most common lithological source rocks for petroleum are carbonates, marine shales and lacustrine shales. Each source rock contains major biomarkers, which then are carried onto its product providing clues to the exact type of source. Lacustrine shales are deposited in significantly smaller areas when compared to marine sources and vary in composition. Much of the source materials in lacustrine shales are terrigenous and more rapidly deposited than marine, unless considering marine shoreline sediments. This rapid deposition leads to greater preservation of material and TOC, which both out pace many marine source rocks, however, lacustrine shales do not show the kind of alteration severity commonly found in marine source rocks making them easily distinguishable from marine sources. Also to be considered when evaluating differences between lacustrine and marine sources are the organic materials, which create definable biomarker, and biomarker ratios from said materials.

3.4.1 Oil Source Rock Type

When evaluating the source rock type, consideration of the kinds and types of biomarkers used should be discussed appropriated to the specific source. Steranes, n-alkanes, isoprenoids and terpanes are highly useful and reliable biomarker identifiers for source deposition. Shale source rocks commonly produce oils that range in medium to high gravities, high amounts of pristane, low amounts of phytane and high amounts of trisnorneohopane (Ts). While carbonate sources encounter medium to low oil gravities, low pristane values, high phytane values and low Ts amounts (Hughes, 1984; Palacas, 1984; Tissot and Welte, 1984; McKirdy et al., 1983; Connan and Dessort, 1987; Connan, 1981; Connan et al., 1986; Riolo et al., 1986; Moldowan et al., 1985; ten Haven et al., 1988 and Fan Pu et al., 1987). High concentrations of homohopanes also suggest either a carbonate or evaporite source, especially when discussing C_{35} homohopane concentrations (Philp and Jones, 1990). In addition, the amount of sulfur produced with oils as H_2S gas can indicate source rock type. Gransch and Posthuma (1974) made the statement that high- and low-sulfur oils originate from high- and low-sulfur kerogens. It was then Tissot and Welte (1984) who made the observation that carbonates have insufficient amounts of metals to use up sulfur deposited with the carbonate, allowing the sulfur to be incorporated into the source rock's kerogen. This is not the usual case for marine shales, which have lots of metal incorporated within themselves, using up the sulfur. Sulfide gas is brought about by the reduction of sulfate anions in an anoxic environment. There are many other parameters that help distinguish between shales and carbonate source rocks, which can be observed in figure 4.

Property	Marine carbonate	Marine shale	Deltaic Shale
API gravity	10-30	25-40	35-45
Sulfur (wt. %)	>0.6	0.2-0.5	<0.2
Saturates/aromatics	0.3-1.5	1-2	>2
CPI	<1	1-1.5	>1.5
Pristane/Phytane	<1	1.1-1.8	2-4
Phytane/n-C18	>0.3	<0.3	<0.1
Steranes	C27>C29	C27<C29	C27<C29
Steranes/Hopanes	Low	High	High
Diasteranes/Steranes	Low	High	High
C24tetra/C26tri	Medium-High	Low-medium	Low
C29/C30 hopanes	High (>1)	Low	Low
Gammacerane/hopane	Low-high	Low	Absent

Table 2. Biomarker table of marine shales, carbonate and deltaic shales. (modified from Peters et al. 2005)

The type of organic matter influences the biomarkers too. The most common types of organic matters are from two differing sources, marine or terrigenous, with both having some distinctive biomarkers. Peters and Moldowan (1993) found that several biomarkers are useful in defining between marine and terrigenous sources, which were used in this study: C_{27} – C_{29} steranes, sterane/hopane, pristane/phytane, pristane/nC_{17} and tricyclic terpanes. Marine sources were found to have high amounts or ratios of C_{28}, lots of steranes to hopanes. Terrigenous sources tend to have >3 pristane/phytane, many C_{29} steranes and many tricyclics. Table 2 lists the biomarker parameters in greater detail and organization. Being that C_{29} steranes are sourced from marine shales and C_{27} steranes are created from terrigenous sources, these two can be used greatly in distinguishing source differences (Edwards et al.,1999).

Ratios between certain tricyclic terpanes are indicative of various source types. C_{22}/C_{21} ratio values above 0.3 tend to be attributes of carbonate sources, while shale sources are lower in value. C_{24}/C_{23} for carbonates tends to be lower than shales, with defining line near 0.7. C_{26}/C_{25} tricyclic ratios are lower for carbonate sources compared to shales. In addition, hopane ratios can indicate a source and even its depositional environment. When $C_{31R}/C_{30\,H}$ values are above 0.35, this indicates a carbonate source, while typical shales have values below 0.35. If ratio numbers are above 0.6-0.7, and greater, for C_{29}/C_{30} hopanes, a carbonate source is likely the culprit. Shale sources tend to depress this value, below 0.6.

Volkman and Maxwell (1986) noted that Pr/Ph ratios under 1 suggests the source rock type as being type I and II; Pr/Ph=1-3 suggests source II type and Pr/Ph=>3 is type III organic matter. Being largely terrestrial in composition, lacustrine sources are more apt to contain C_{26}/C_{25} tricyclic terpanes >1 as found by Zumberge (1987a) and to have elevated tetracyclic rations according to Holba et al. (2000) from land plants.

3.4.2 Oil Source Rock Maturity

An important parameter influencing crude oils' geochemical characteristic is the age of the source rock. The thermal age of a source plays a dramatic role on the kinds of petroleum produced out of a source rock, the availability of resources and duration left for petroleum to be produced. Biomarkers carried over to the oil from the source clue geologists as to that theoretical age of the source and what the possible expectations are left towards the source. According to Moldowan and Peters (2003) petroleum source rocks are described on quality, quantity and thermal maturity of the organic matter. Organic matter age is described on the thermal maturity scale as immature, early mature, peak mature, post-mature and condensate (Tissot and Welte, 1984) where immature sources see little influence by heat, but more from organic amounts and type. Mature sources are much more influenced by heat than immature ones, largely by catagenesis, which Moldowan and Peters (2003) define as the oil-generation window. Postmature sources are beyond the peak oil-generation window, where more oxygen and less hydrogen are present, eliminating the opportunity for petroleum generation, but can still produce gas.

Terpanes are highly useful biomarkers when it comes to determining source rocks thermal maturity. By using the m/z 191-gas chromatogram, picking certain peaks and their associated areas will point towards a maturity parameter. Siefert and Moldowan (1980) found that certain ratios of these C_{31}-C_{33} homohopanes (C22S and C22R) indicate the age of the source: if the ratio is 0.50-0.54 then it is early into oil generation; 0.57-0.62 means the source has reached max oil generation or just passed this supposed peak. A homohopane is the ratio of C22S to C22R, where C22S is a geological alteration of C22R, a biological input. What occurs is the rotation of the alkyl chain at the C22 site from a right to left (sinistril), or R to S. Hansen et al (2007) used the reverse ratio and discovered that when the peak oil generation window has been reached, the ratio reaches a 3:2 value that will not change with greater thermal maturity. Seifert and Moldowan (1978) also gave major credence towards tricyclic terpanes abundance when compared to C_{30} 17α-hopanes because it was found that as a source matures, the tricyclic terpanes amount increases (Aquino Neto et al., 1983).

Van Graas (1990) determined that concentration of hopanes, and Ts/(Ts+Tm) can be used in oils produced from very mature source rocks. C_{27} 18α-trisnorneohopane (Ts) and C_{27} 17α-trisnorhopane(Tm) concentrations can be affected by source type and source maturity (Peters and Moldowan, 1993; Zumberge et al, 2005). This ratio is useful do to the fact that Ts is less stable at higher temperatures than Tm, and it is during catagenesis that the Ts are converted to Tm, giving higher values of Ts/Ts+Tm (Seifert and Moldowan, 1980). Seifert and Moldowan (1980) stated that the ratio of moretane/ C_{30} hopane is useful for maturity evaluation because as a source thermally matures, the moretane is converted into C_{30} hopane. Hopane (17α, 21β(H)) values can also come from the thermal conversion of moretane (17β, 21α(H)). Moretane comes about from the alteration of other 17α-hopanes (Peters et al., 2005) through a series of Gibbs free energy reactions. Both 17α, 21β and 17β, 21α hopanes are created from the biological 17β, 21β hopanoid, but because of the ease of creation for 17α, 21β hopane, all will be converted through enough heat. Mackenzie et al.(1980), and Siefert and Moldowan (1980) found that thermally mature oil sources will have very low moretane/hopane ratios, where peak oil values reach 0.15-0.05, while immature oil values are ~0.8, where moretane is slightly source dependent, but not substantially.

Steranes are also used to distinguish the thermal maturity of a source rock. By investigating the quantitative values of the sterane (m/z 217) gas chromatogram for the ratio of the C_{27} αααS/C_{27} αααR+C_{27} αααS, and the same for the C_{29} sterane, a source maturity range can be determined. If the ratio values fall within the 0.23-0.4, the source has reached early oil-generation stage, while a value of 0.4-0.55, the source is in the peak oil generation stage. As a source matures further, the amount of the biomarker C_{27}S diasterane is increased from the conversion of C_{27}R, while the concentration of C_{27}R sterane is diminished do to the same reasons as for the diasteranes.

There are other ways to evaluate a sources age, other than by looking at certain biomarkers. One area that should be paid attention to is the amount of biomarkers responding in a gas chromatogram. Mackenzie et al (1985) found that the less mature a source, higher concentrations of biomarkers are found, while vice versa, the lower the concentrations, the more mature a source. In addition, only certain types of biomarkers and ratios can be used up to certain points, when identifying the source age. Comparison of isoprenoids ratios from the whole oil gas chromatogram is one, where the value will increase with increasing source maturity (Alexander et al. 1981). Another was is to investigate the number of hydrocarbon chains to each other by comparing the preference of oil for either odd or even chains, as used by Bray and Evans (1964). If the value is highly above or below 1, then the source is thermally immature. If the value comes out near 1, then this suggests the petroleum source rock is thermally mature.

3.5 Oil Alterations

Petroleum commonly encounters many alterations follow expulsion from its source, with the most usual forms being biodegradation, and water-washing. Both of these occur in the subsurface, but are susceptible and influenced in only restricted systems and environments. Biodegradation can only occur in areas where life can be sustained, which needs food, water, correct salinities and pHs. Water-washing can only take place when petroleum is in direct contact with water.

3.5.1 Water Washing

Water washing can take place at several stages on oils, altering the oils in preferential fashion, and at different stages. According to Lafargue and Barker (1988) waters tend to remove only certain hydrocarbon chains, the more soluble, polar compounds. Given that water is one key ingredient for microbes in reservoirs to live, water-washing is usually accompanied by biodegradation and is overshadowed by the biodegradation. Water washing has been observed to occur at different stages, when the oil migrates to the reservoir and when the oil is resting in the reservoir.

As stated before, certain hydrocarbons are preferentially dissolved by water do to their polar attributes. Like many learn in chemistry, "like dissolves like" giving rise to ask what compounds are likely to be removed. From McAuliffe (1979) and with additions by Price (1976) it was found that shorter hydrocarbon chains are much more soluble than longer ones, where aromatics are the mostly likely to dissolve first. N-alkanes 15+ show dramatic loss when contacted with water. Some major aromatics to pay attention to are the methylphenanthrenes, which is removed later on by waters, and pristanes/ and phytanes showing increased concentrations. API gravities in Lafargue and Barker's (1988) experiment are only slightly affected as indicated by the gravities decreasing from 36 to 31.

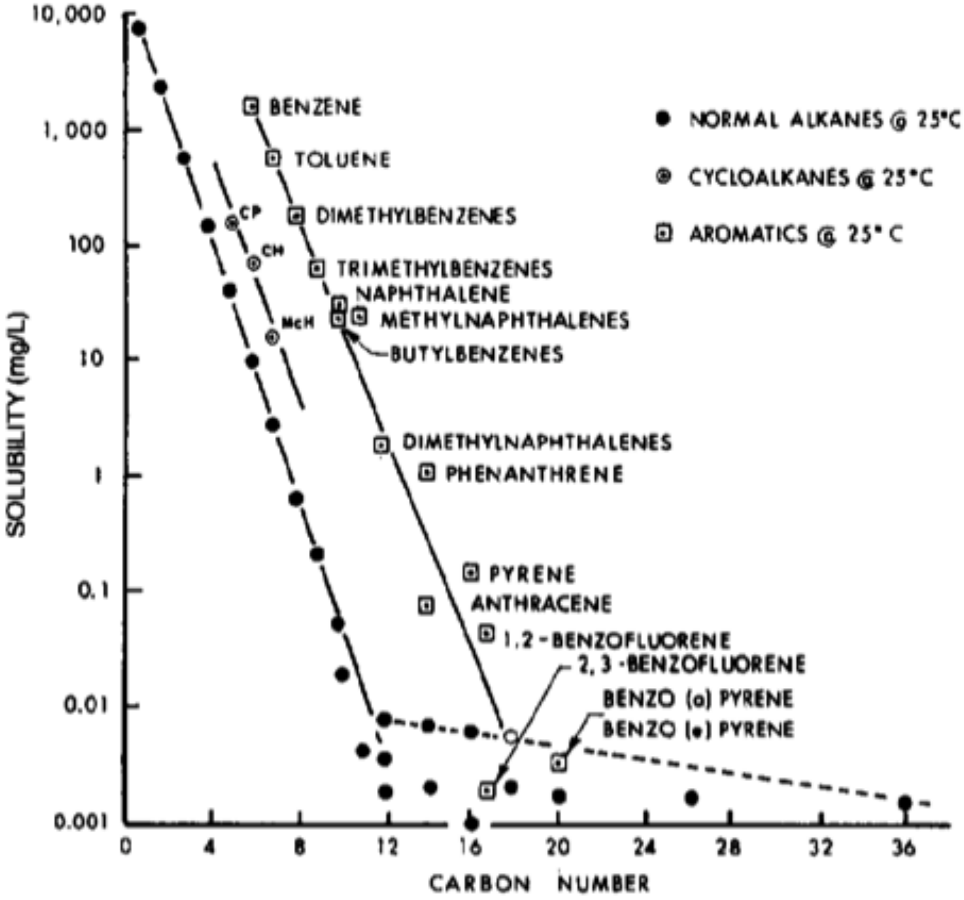


Figure 3. Solubility figure of aromatics, paraffins and naphthenes in water as a function to carbon number. (Lafargue and Barker, 1988)

3.5.2 Oil Biodegradation

As previously stated the biggest influences for biodegradation to occur at the correct environment: nutrients, temperature, salinity, pH and pressure. Moldowan and Peters (2005) discussed that for an organism to break down oils as a food source it can be done in more than one way. Some microorganisms have been known to secrete biosurfactants for cellular breakdown, the creation and use of enzymes and biopolymers, which can transform oils into water-soluble compounds. Some microorganisms may convert the oil in carbon dioxide, water and nutrients via oxidation, while another may use nitrates, sulfates and ferric ions to break down the hydrocarbon.

Reservoir temperatures can play a large influence on the presence and type of organisms living in the subsurface. The most beneficial temperatures for organisms are near-surface ones, where 60-80 degrees Celsius is the ceiling for many microbes as observed by Shi Ji-lang et al. (1982) when biodegraded oils in China occurred at temperatures no greater than 70 degrees Celsius or deeper than 1500m. However, these conditions may have not occurred consistently through time or reservoir filling. Peters and Moldowan (2005) noted that the South Timbalier Field in the Gulf of Mexico currently has reservoir temperatures greater than 90 degrees Celsius, but has oil-showing biodegradation. This may have occurred from post-filling tectonics and subsidence increasing the reservoirs temperature overtime.

Salinity of reservoir fluids must be given much consideration when understanding biodegradation. Many observations by geologists indicate that biodegraded oils occur in waters with low-salinity (<100-150 ppm). However, some organisms are capable of surviving salinities higher than these values. Roessler and Muller (2001) decreed that there are some domains of life that can withstand highly saline environments by regulating their internal osmotic pressure by amassing solutes internally. This includes halophilic (sulfur bacteria, green algae) microorganisms, which live in water with salinities >100-150 ppm, a common salinity in both hypersaline marine and high-alkaline environments (Kirkland and Evans, 1981) suggesting that halotolerant microorganisms could occur in carbonates and evaporate source and reservoir rocks. When discussing the pH of reservoir brine, consideration must be given to the amount of hydrogen sulfide, a byproduct of sulfate reduction. H_2S and CO_2 both act as acid gases in reservoirs, but are buffered by reservoir rock mineral reactions. This allows for milder pH's and allows for pH tolerant microbes to survive, breaking down oil. Reservoir pressures seem to play much less influence on life in the subsurface as observed by Sharma et al. (2002), Moldowan et al. (2002) and Walters (1999). All observed very high pressures, even reaching 1680 MPa and depths as deep as 4000 meters, which is all cases reservoir temperatures were maintained around 80 degrees Celsius.

Biodegradation can affect oils physical and molecular properties, a fact that is well known in exploration (Connan, 1984; Peters and Moldowan, 1993; and Peters et al., 1996). Biodegradation appears to occur in a mode of "quasi" steps (Seifert and Moldowan, 1979) where only certain biomarkers are consumed following others biomarkers. Case in point, aromatic and saturated biomarkers are biodegraded prior to n-alkanes and simple branched alkanes. These are then followed by regular steranes, hopanes, diasteranes and tricyclic terpanes. All of these steps can be interpreted cautiously by quantitative analysis of peaks and peak ratios along with qualitative analysis. Comparison of known peaks in one well's chromatogram to another is the most practiced means of qualitative analysis.

When microbes consume oil, they have a preference for certain hydrocarbon chains, typically removing C_6-C_{12} n-alkanes initially, which can be qualitatively observed in gas chromatograms. Observed in these chromatograms is that as oil biodegradation progresses the lower end n-alkanes are removed, followed by the noticeable isoprenoid alkanes peaks being maintained throughout (Horstad and Larter, 1997). In addition, a prominent "hump" begins to grow larger and larger as the alterations increase with more and more higher end alkanes diminish. This hump is referred to by the UCM or unresolved complex mixture, being made up of the bioresistant compounds which includes highly branched and cyclic saturates, and aromatics (Peters and Moldowan, 2003). These steps are referred to as the Biomarker Biodegradation Scale by Wenger et al. (2002) and provides for a novice ranking system for level of biodegradation, along with a pseudo-order list from Moldowan and Peters (2003). (Table 3).

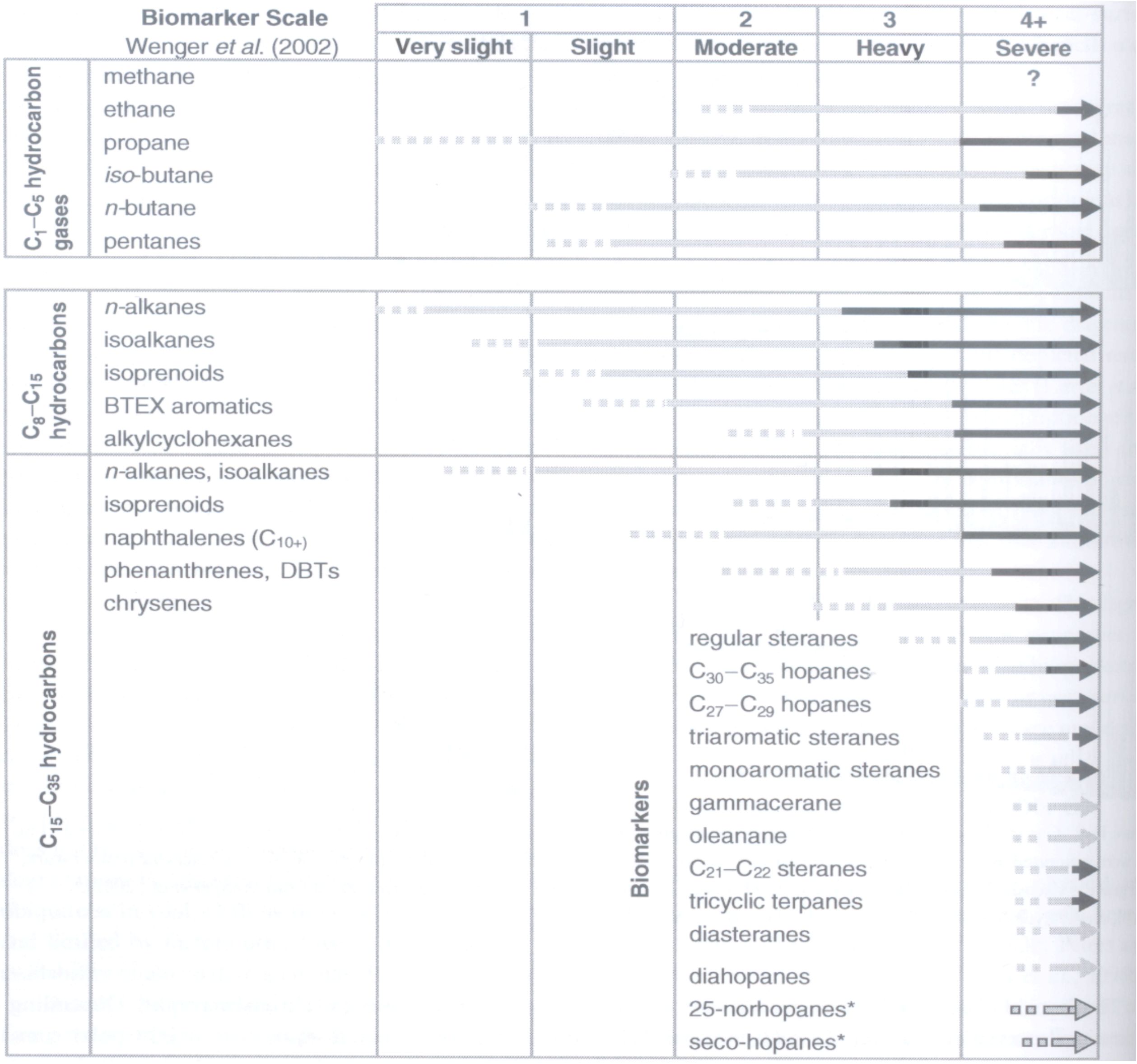


Table 3. Biomarker biodegradation scale. Indicates sequence of the removal of groups at increasing levels. First alteration is dashed line, highly altered is solid gray, and completely eliminated is solid black. (Peters et al. 2005)

The m/z 83 chromatogram is helpful in illustrating whether biodegradation has occurred. The m/z 83 chromatogram measures the hydrocarbon chains called n-alkycyclohexanes. When biodegradation occurs, these biomarker increase in amount following the near depletion of the n-alkanes (Peters and Moldowan, 2003). Initial values of these biomarkers in non-biodegraded oils have higher amounts of the n-alkanes that have the greatest retention times. Partial degradation removes these biomarkers, and in greater degraded oils, these biomarkers are highly depleted, but early retention biomarkers, the alkycyclohexanes increase (Figure13).

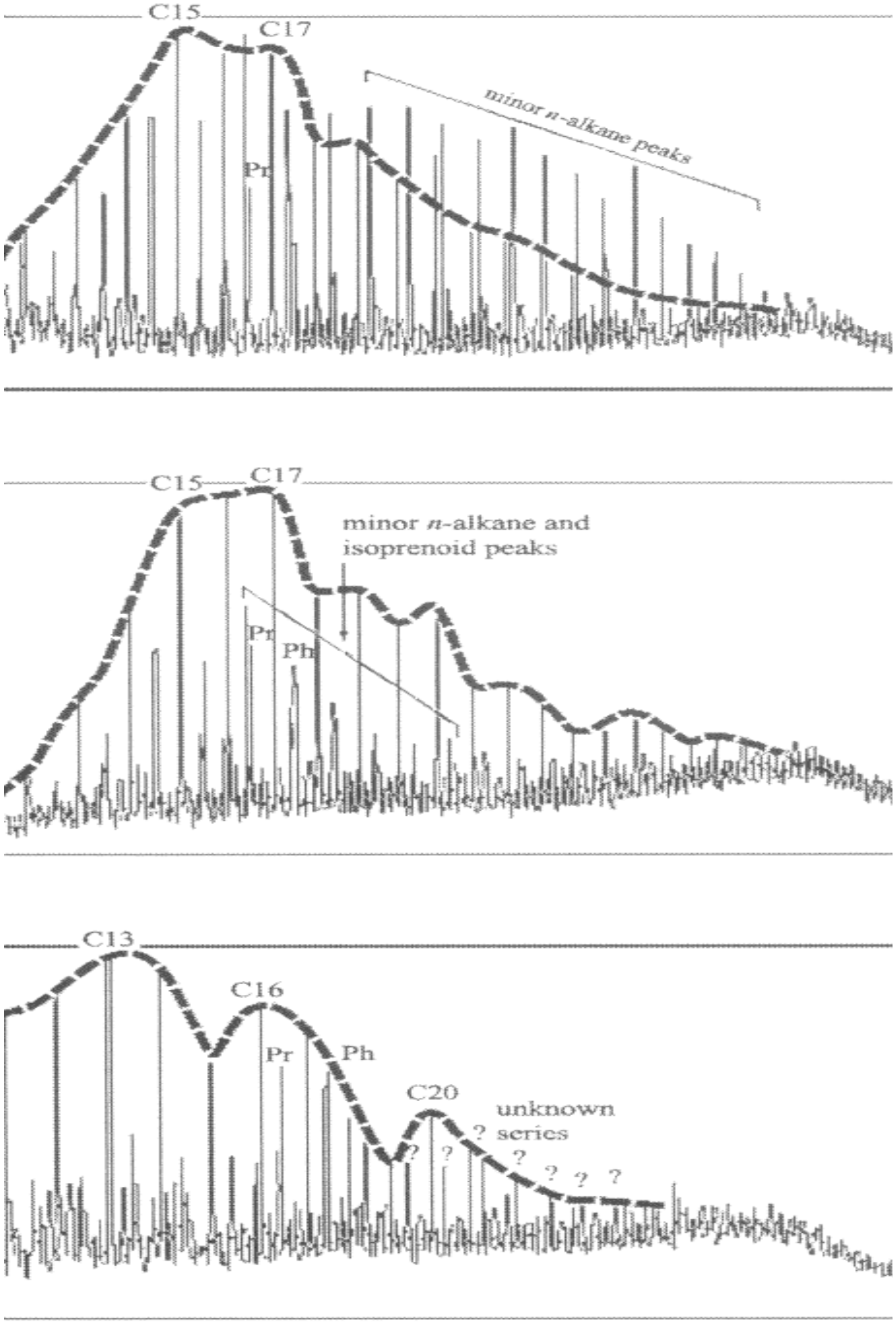


Figure 4. M/Z 83 gas chromatograms showing the effects of biodegradation with increasing alteration (top to bottom). (Peters et al. 2005)

Under prolong exposure to microbes and the effects that they bring about, an overall understanding should be discussed. As stated in the previous parts of the chapter, microbes will consume the hydrocarbon chains, changing the oils composition, but will also change the physical make-up. As the consumption continues, the oil will become heavier and heavier in density and more enriched with nickel, sulfur and vanadium, indicating alterations. Also, when considering an oils alteration and characteristics gas-to-oil ratio (GOR) values are important in understanding what effects are influencing and controlling these values. Arouri et al (2010) stated that thermal maturity and type of source rock, the charge history and the regional distribution of the carrier, reservoir and seal bed influence GOR distribution in a field. However, this only controls initial characteristics of the GOR, when obviously alterations will occur post accumulation. Sited by Arouri et al (2010) are water-washing, oil cracking, biodegradation, segregation, and phase separation caused by pressure drop or gas influx. When gas migrates into a laterally extensive reservoir, it has the habit of displacing oils into shallower areas (Gussow, 1954). According to Gussow's principle, API gravity and GOR increases towards the basin's center. In addition, preference by microbes and water for the lighter end n-alkanes tends to decrease oils GOR, where the lighter end alkanes tend to compose natural gas.

Chapter 4-

4.0 Materials and Methods

For longevity in many careers, especially in petroleum exploration, the summation of many disciplines is key. Therefore, the incorporation of geochemical, mineralogical, and stratigraphic data was utilized to benefit this study. More specifically, geochemical data, core samples, well-cuttings and well-logs were used to assess the possibility of compartments in the Pineville tripolite facies in Spivey-Grabs-Basil Oil Field. All of the geological data analyzed for the study was from the subsurface, exclusively from wells drilled into the formation of interest. For analytical work, one core nearest to the area of interest was used for analysis, along with well-cuttings from wells drilled in the area. Eleven oil samples were collected and sent to the University of Oklahoma for biomarker analysis.

4.1 Sedimentology

The formation of chert is a highly debated subject, having many conflicting explanations. Agreement is reached when discussing the rock being precipitated out of solution, but the peace is short lived when discussion turns towards the source of the silica ions. For the sake of argument and the topic of this thesis, the hypothesis of the Pineville Tripolite facies will not be discussed in-depth, only superficially. When pondering the Pineville Tripolite facies, discussion is turned towards the spatial and temporal relationships among the Mississippian and Pennsylvanian rocks in the study area, including depositional environment. Sedimentologic and stratigraphic characterization of the Pineville Tripolite was determined by subsurface techniques. By using petrophysical logs (spontaneous potential, gamma ray, neutron porosity, density porosity, and electrical logs) Pineville lithofacies was achieved, with the construction of cross-sections from these well logs provides a facies pattern, regional perspective and stratal geometry.

4.2 Gas Chromatography/ Mass Spectrometry

The use of gas chromatography-mass spectrometry (GCMS) is widely used in today's industry to evaluate source rocks and oils. It is also used outside of the industry by law enforcement and other disciplines to analyze drugs, medicine and other forms of organic compounds. With a GCMS, one can identify many compounds based on retention time and upon structure characteristics. When evaluating biomarkers, computerized GCMS is the primary method (McFadden, 1973). According to Moldowan, et al. (2005) six tasks are performed when running a GCMS system: 1) Compound separation. 2) Movement of separated compounds into ionizer. 3) Ionization. 4) Mass analysis. 5) Ion detection via electron multiplier. 6) Acquisition, processing and display of found data by computer.

In order to analyze samples, an injection by syringe of a known amount of oil is placed into the gas chromatograph, either mixed with helium or hydrogen. Helium is the more desired gas because of its inert qualities, providing more precise results. Upon injection, the oil sample is vaporized continuing into a capillary where the oil separates into differing biomarkers due to their physical characteristics at different times and recorded.

Mass spectrometry is achieved when electrons are sent into a molecule forcing the ejection of hydrogen, making the molecule unstable, creating either a positive (+) or negative (-) molecule, depending upon the charge, the molecule will flow past an electrode where its weight to charge will be measured. The charge is commonly one for the molecule, so the mass is the item being measured. Measurements are achieved from calculating the abundance of the biomarker molecules, each having their own specific weight and bonding characteristic. Based upon these two criteria, molecules will react at different times to the heat source.

Samples were run through an Agilent Technologies 5957c GC analyzer that was set to a sampling time of 100 minutes where initial temperature was set at 40 degrees Celsius and reached a maximum temperature of 300 degrees Celsius. Oil samples were injected from a syringe with oil volumes at 10 milliliter in to a capillary column having a constant flow rate of 1.4 mL per minute at 21.725 psi, having a velocity through machine averaging 30.339 cm/sec. The mass spectrometry analyzer was running the same volume as the GC, where the electro-magnet was running on 2435 volts. During the analysis, oil was charged and measured at the masses of 83 (n-aklylcyclohexanes), 85, 110, 123, 124, 177, 183, 191 (terpanes), 205, 217 (steranes), 218, 231, 232, and 253. The MS source temperature reached 250 degrees Celsius, while its quad achieved 200 degrees Celsius. Samples were analysis from the 10-minute mark to the 100-minute mark. These Gas Chromatograms can be seen Appendix A.

4.3 Oil Sampling

Eleven oil samples were gathered from the wellheads of ten different well sites with the verbal permission of Pickrell Drilling Co., Edmiston Oil, and Vess Oil Co., with the help from Deom Howard. Collected oils were placed in glass jars and were immediately capped and placed in an ice chest. All samples were transported back to Kansas State University, the whole time kept in a cold environment. Following 2 weeks of resting in a refrigerator the samples were safely packed into a chilled cooler and shipped to the University of Oklahoma for gas chromatograph/mass spectrometry analysis. Gas chromatograms are found in Appendix A.

Chapter 5 –

Results

5.0 Oil Properties

The following sections chart detailed geochemical characteristics of the Mississippian Tripolite facies oil. I readily agree with Dr. Philp (personal communication, 2010) that analysis of oils can greatly benefit geologists in understanding an oil field's history, source, and dynamics. Complexity of oils is a considerable making analysis a daunting task, but fruitful results will follow even if they are not as expected. The main aspect for oil geochemical analysis is the use of gas chromatography and biomarker ratios (Table 4).

Name	API Number	C24tri/C23tri	C31r/C30H	C26tri/C25tri	Ts/Ts+Tm	C31s/s+r	C32s/s+r	C33s/s+r	C30m/C30H	C29t/C29H	C29/C30	C22t/C21t
Pound 1	1509500754	.7	.29	.4	.26	.61	.59	.58	.09	.08	.75	.28
Krehbiel B	1509501798	.7	.31	.42	.26	.6	.6	.58	.09	.08	.65	.27
Voran 1-35	1509521952	.69	.31	.41	.28	.6	.6	.59	.09	.09	.78	.28
Spring Acres	1509530071	0.69	.29	.42	.27	.61	.6	.59	.09	.09	.73	.28
Sullivan 2	1509520450	0.69	.29	.4	.27	.61	.6	.6	.09	.08	.72	.31
Bruch 1	1509501780	0.69	.31	.42	.27	.61	.6	.59	.1	.08	.76	.27
Bruch 2	1509522118	0.69	.31	.4	.27	.6	.6	.59	.09	.08	.76	.28
Maple 2E	1509520210	0.69	.31	.42	.26	.6	.6	.6	.09	.08	.66	.28
Maple F1	1509500720	0.70	.31	.65	.25	.6	.6	.6	.09	.09	.66	.29
Maple F2-3	1509522204	0.70	.31	.64	.31	.59	.59	.59	.11	.08	.76	.32
Maple F2-4	1509522204	0.72	0.31	.67	.3	.5	.59	.6	.11	.07	.75	.17

Name	API Number	C27%	C28%	C29%	C29s/s+r	C29 bb/(bb+aa)	C27d/C27d+C27r	C29/C29+C27	29bbR/29aaR	29aaS/29aaR
Pound 1	1509500754	0.31	0.24	0.44	0.49	0.60	0.27	0.56	1.67	0.99
Krehbiel B	1509501798	0.30	0.24	0.46	0.45	0.56	0.27	0.58	1.35	0.83
Voran 1-35	1509521952	0.30	0.24	0.45	0.43	0.57	0.27	0.57	1.38	0.81
Spring Acres 1	1509530071	0.30	0.24	0.46	0.44	0.57	0.27	0.58	1.37	0.81
Sullivan 2	1509520450	0.31	0.24	0.45	0.48	0.58	0.27	0.56	1.60	0.99
Bruch 1	1509501780	0.30	0.24	0.45	0.45	0.57	0.27	0.57	1.38	0.81
Bruch 2	1509522118	0.31	0.24	0.44	0.48	0.58	0.27	0.56	1.62	1.02
Maple 2E	1509520210	0.30	0.23	0.46	0.46	0.55	0.27	0.58	1.34	0.86
Maple F1	1509500720	0.31	0.24	0.44	0.51	0.59	0.27	0.56	1.66	1.00
Maple F2-3	1509522204	0.31	0.24	0.44	0.49	0.59	0.28	0.55	1.65	0.97
Maple F2-4	1509522204	0.3	0.26	0.43	0.50	0.59	0.28	0.56	1.67	1.00

Table 5. Terpane Ratios, top. Sterane Ratios, bottom.

5.1 Oil Biomarkers and Geochemistry

The oil produced out of the wells is typically hot, black, and have a distinct smell. API gravity's range from 28-37 degrees in the study area, but the gravity's of the oils sampled were less varied, ranging from 32-37. Production of sulfur occurs locally with the some wells in the study area at levels lethal enough, requiring the presence of warning signs at well sights. Production from these wells is some what contrasted in volume and in type. Wells here are known to produce high amounts of water, oil and gas providing many questions to be raised.

5.1.1 Gas Chromatogram Analyses

Eleven oil samples from ten different wells were analyzed for biomarkers by gas chromatography and mass spectrometry. 40 peaks were identified in all the samples as denoted in table 5, showing the peaks identified in the samples. Samples were chosen from wells producing from only the Mississippian formation, where the samples produced at the top-most depth of the formation. Formation depth is varied throughout the study area, so any variations may be explained from these depth changes.

The 40 peaks that were picked are more correctly called oil biomarkers. Notable biomarker families used were n-alkanes (Figure 17), steranes (Figure 16), terpanes (Figure 15) and the n-alkycyclohexanes (Figure 21). Those biomarker families are broken into individual biomarkers. Analysis of the peaks pertained to the areas and peak height of each individual, and these values were placed in several different ratios for source maturity, source type and oil alteration. Area was calculated by taking the product of the peak height and half-height peak width. Peak positions for hopanes 29, 30, 31S and R, 32S and R, 33S and R are located in on the m/z 191 gas chromatogram at times 70.269, 72.155, 74.71, 75.044, 77.049, 77.574, 80.269, 81.155, respectively. Other terpane peaks allocated to the m/z 191gas chromatogram are the C_{22}-C_{29} tricyclics at 51.888, 55.779,56.877, 59.145, 64.444, 65.471, 66.927, 67.739, and 69.362, respectively (Figure 15) (Philp, 2011).

Sterane peaks used in this investigation are identified (Table 6) listing the peaks on figure 20. The peaks used were the C_{27-29} cholestanes, C_{27} diasteranes and the C_{20-21} steranes. Times for these peaks are 54.1, 55.8, 62.7, 63.3, 65.5, 65.65, 65.8, 66.2, 67.6, 68.7, 68.9, 69.1, 69.8 and 70.7.

Table 4. n-Alkane and Isoprenoid Values for Figure 17.

	Peak Name	Pr/Pr+Ph	Pr/Ph	Pr/n-C17	Ph/n-C18	CPI
Pound 1	Pr=Pristane	0.593	1.460	0.443	0.395	1.002352941
Krehbiel B	Ph=Phytane	0.536	1.155	0.451	0.390309556	0.857909532
Voran 1-35	n-C_{17}	0.542	1.183	0.438	0.374045802	0.902855057
Spring Acres	n-C_{18}	0.546	1.202	0.414	0.360515021	0.896946565
Sullivan 2		0.531	1.134	0.433	0.393939394	0.880275367
Bruch 1		0.539	1.170	0.446	0.38630137	0.900268817
Bruch 2		0.532	1.14	0.439	0.381679389	0.93840687
Maple 2E		0.536	1.157	0.479	0.41010101	0.872645064
Maple F1		0.521	1.089	0.454	0.445714286	0.839378238
Maple F2-3		0.510	1.043	0.458	0.464882943	0.794198895
Maple F2-4		0.502	1.011	0.283	0.268181818	0.782306163

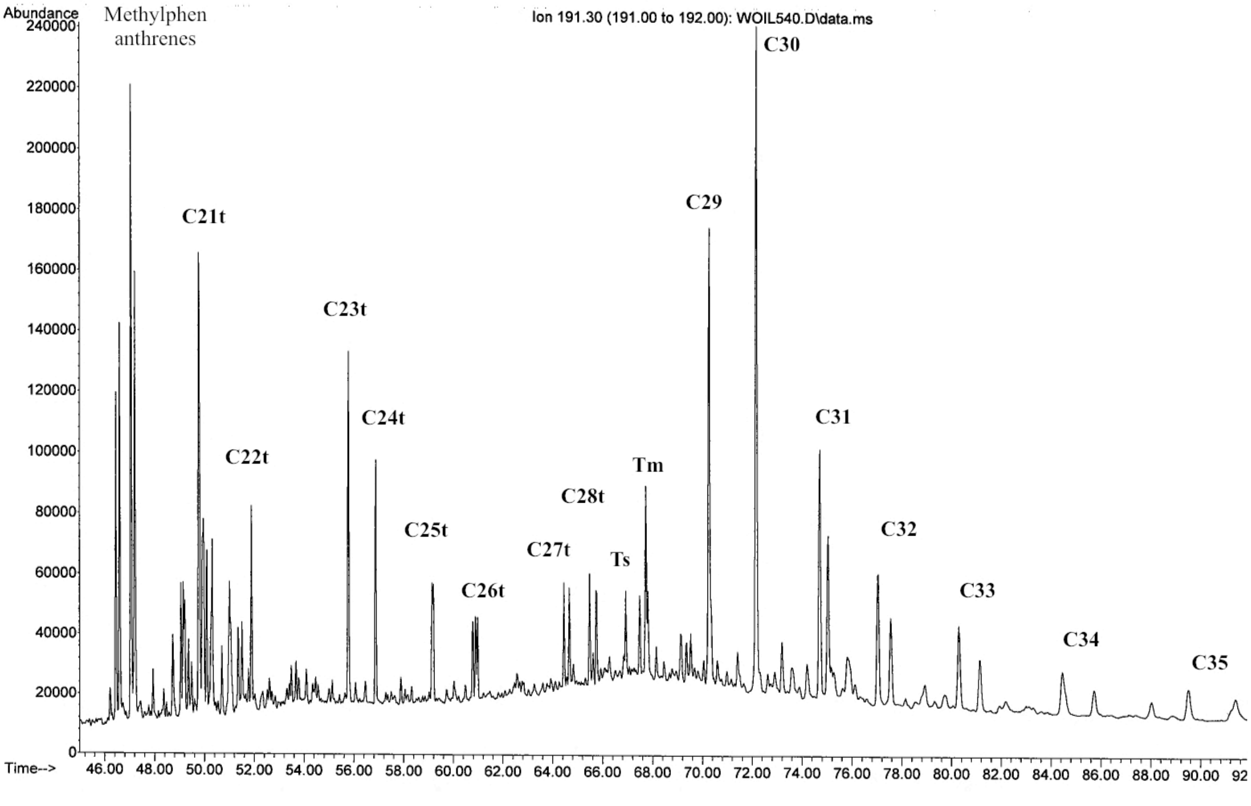


Figure 6. M/Z 191 Gas Chromatogram with biomarkers picked.

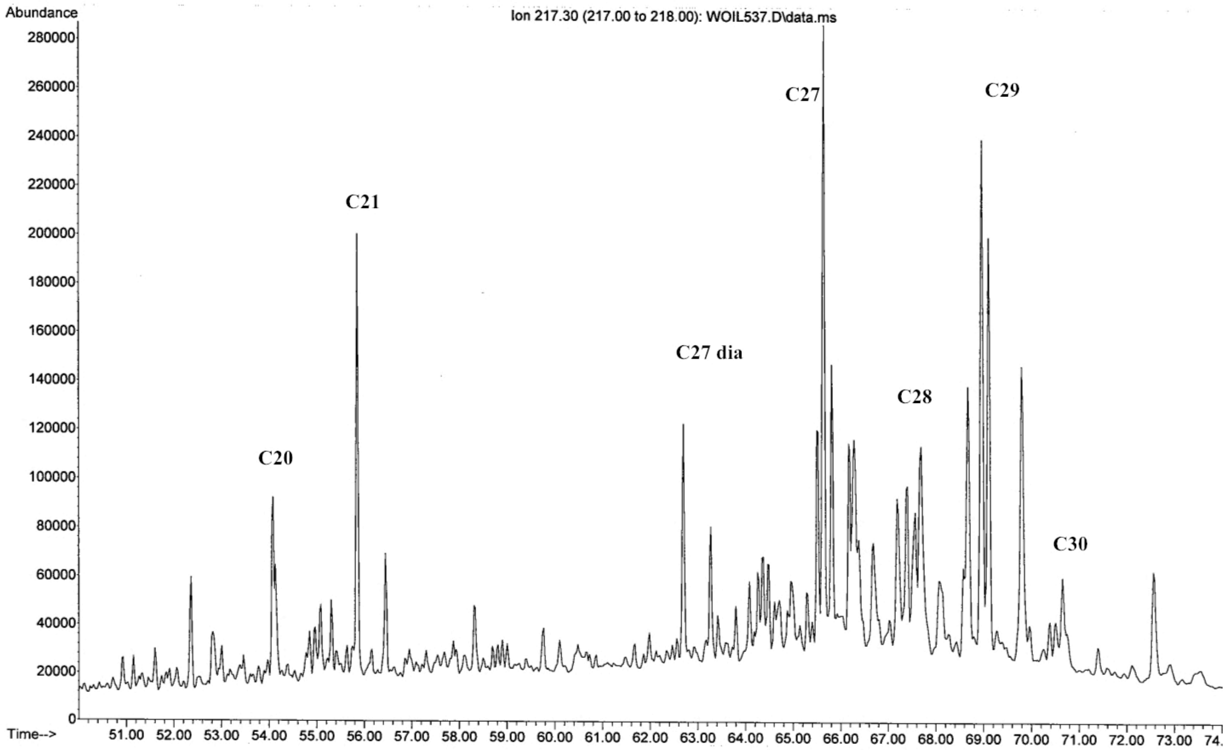


Figure 7. M/Z 217 gas chromatogram with peaks picked.

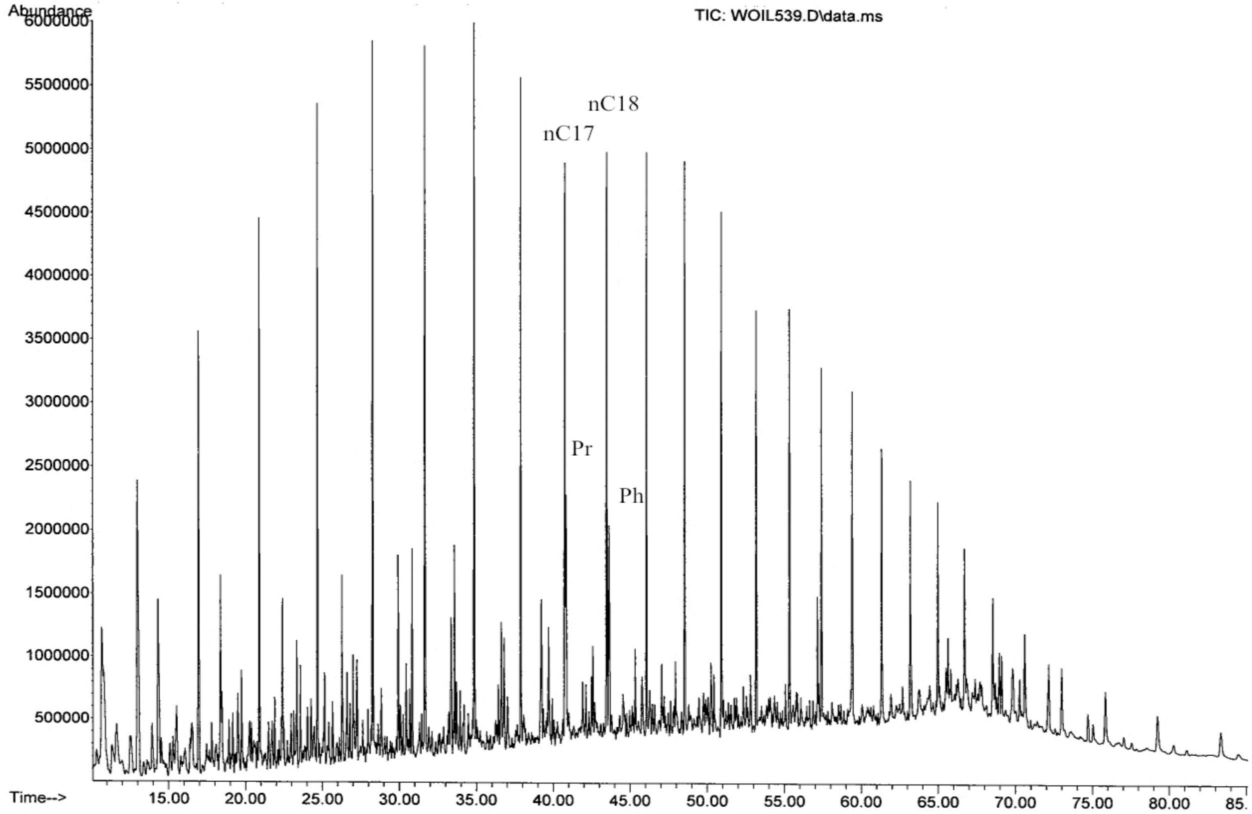


Figure 8. TIC gas chromatogram with nC17-18 and Pr, Ph identified.

5.1.2 Oil Source Rock Type

The bulk of the oil wells were located in section 25, T29S R7W in the Basil area of the Spivey-Grabs-Basil oil field. Production is out of the Mississippian Pineville Tripolite facies, where oil, gas and water are produced. Biomarker evidence can show several indications and suggestive evidence about an oils source rock type (Tables 4 & 5). Terpanes, steranes and other biomarker are the most commonly used ones used to delineate a source as being marine or terrestrial, shale or carbonate and even anoxic or oxic. From the sterane biomarkers values, the oil has large percent of C_{29} steranes (45%), and C_{27} steranes (33%). There is data pertaining to the diasterane/sterane ratio where accordingly low amounts of diasteranes present in the chromatogram indicate a source that is carbonate in type. Terpane amounts and chromatograms signify that the source rock is marine shale because of the low C_{22}/C_{21} tricyclic terpane ratios and high C_{24}/C_{23} tricyclic terpanes, but tricyclic terpanes are affected by source maturity (Figure 21). C_{31} R/C_{30} hopane ratios reached on average 0.30. Two ratios do narrow down the source to one specifically, those two being the C35/C34 and C29/C30 hopanes whose values reach >0.8 and 0.7, respectively. In addition, when comparing the Pr/n-C_{17} to Ph/n-C_{18} the amounts reach an average of 0.43 and 0.38, respectively (Figure 22). The source rock environment is indicated by the pristane/phytane ratio, which is slightly above one. Carbon Preference Index for these oils shows a preference for odd carbon chains.

5.1.3 Oil Source Rock Maturity

Biomarkers indicate the maturity of a source rock from various ratios and values whether the source is immature, early, peak, late or condensate (Table 4 & 5). Ts/Ts+Tm ratios are one commonly used for source maturity evaluate and their values reached 0.27. The C22s/C22r+C22s, moretane/hopane ratios and the abundance of tricyclic terpane abundance in the gas chromatogram all indicate the source's maturity to, where C22s/C22r+C22s = 0.59 (Table 4), moretane/ hopane = 0.08 and value of C29 steranes ranging from 0.40-0.5. From the peak amounts and qualitative analysis of tricyclic terpanes on the m/z 191gas chromatogram, its values appear high, a convenient way of maturity evaluation. As observed in the odd to even predominance value, being that the values are close to the value of 1.

Noticeable influence was observed in the individual biomarkers concentrations (Appendix A). As noted by Mackenzie et al. (1985) this is one way to understanding the maturity of the source when the oil was expelled. They observed that a mature source creates oil biomarker concentrations lesser than oils created in younger sources. Analysis of the C_{29} isomers shows two main groups of maturity for the wells tested. One group is shown to be slightly less mature than the other one. Biomarker evidence indicates variations in thermal maturity within the study area.

5.1.4 Alterations

Gas chromatograms of all the oil well can reveal if an area has received little or no biodegradation. Signs from the m/z 83 gas chromatograms indicate this where the Krehbiel B1 and Maple F1 wells appear to have encountered no biodegradation, while all the other wells do show microbial activity has stripped away the n-alkanes (Figure 21). Stimulation methods on Maple F2 and Sullivan 2 produced non-useable m/z 83 chromatograms. The presence of many of the heavy, high-end biomarkers in the m/z 191 and 217 chromatograms and the presence of methylphenanthrene (Figure 15), these being one of the first, are indicative that areas of biodegradation received very slight-to-slight influence from the microbes.

5.1.5 Oil – Oil Correlation

For oil-to-oil correlation to be feasible, a couple of parameters must be met 1) discerning oils from source and 2) defiance of the oils against biodegradation and thermal alterations. As discussed verbally with Dr. Philp, for any compartmentalization study to be achieved initial analysis of the gas chromatograms is needed to determine if oils of a said area are sourced from the same rock by comparing bulk chromatogram qualitatively (Appendix A). This is sometimes difficult do to source biomarkers are susceptible to thermal maturity and biodegradation changing quality. Upon identification of this fact, biomarker analysis and ratios are needed because of their resistance to post accumulation alteration on their structures. Quantitative analysis of biomarkers for same source oils will tell the geologist about the type of source, the age of source and the environment of deposition.

5.2 Compartments

Once a common source rock is determined, ratios and volumes of biomarkers can help determine compartments based upon fluid compositions. For this study, biomarker analysis and composition of the oils was used to help determine or even imply the possibility of compartments. In addition, density porosity and resistivity well log analysis was used to determine structural and isopach values, which can aide in compartment identification.

5.2.1 Biomarkers

As observed from the Biomarker Maturation Index (figure 19 & 25), there appears to be two distinct source rock maturities for the area of study: a mature and less mature source. As illustrated by the BMI chart and well location map, several areas within the field have distinct differences in maturity. Peters et al. (2003) stated that while a reservoir fills, if mixing of the oils is not allowed, this is indicative of compartments and this can create separation between the oil types. If this does happen, especially where different maturities are found, the less mature oil is assumed to have migrated further than the more mature oil. This fact of segregation is observed in the study area, with the lack of biodegradation may indicate that this field filled at different times from the same source rock. The other biomarker quantities show little indication of compartments, but indicate that all oils are from the same source.

5.2.2 Isopach and Structure Maps

Isopach maps indicate separation of different areas where the maturities are also separated out. The Voran 1-35 well has a thin northeast of its location and has different maturity values from the Sullivan 2 and Pound 1 wells, the closest neighboring wells. Sullivan 2 is also different of maturity from the Krehbiel 1 well, located north of Sullivan 2. Between these two wells is a isopach thin, possibly separating the two. In sections 25 and 24, there are distinct maturity variations, but little evidence from the isopach of lithological barriers. The Bruch 2, and Maple F1 and F2 wells show strong maturity correlation, but few similarities to the Bruch 1, Maple E2 and Spring Acres wells. None of these wells are indicated to be separate from each other by a barrier, yet there are differences between them, (Figure 18).

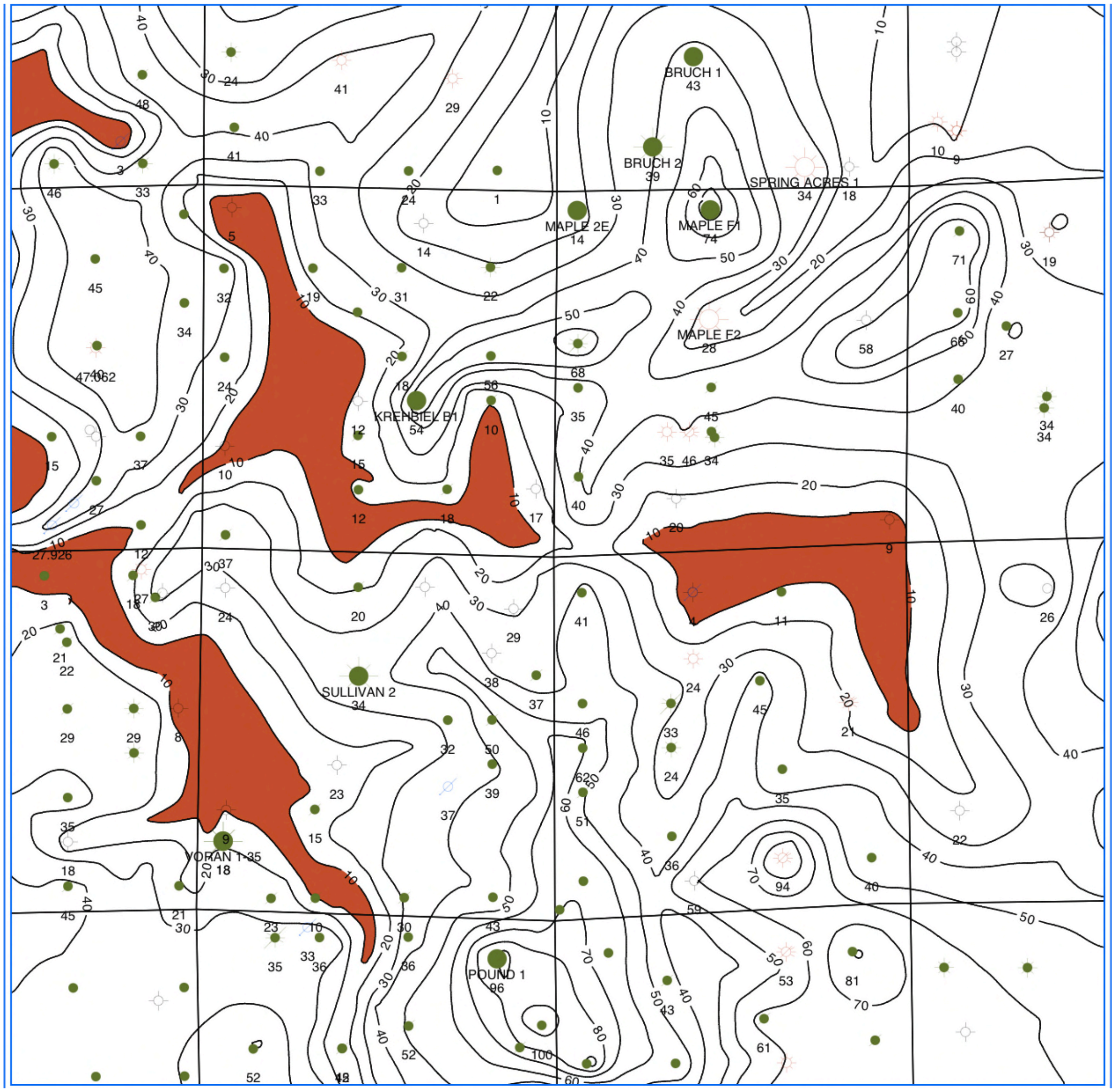


Figure 9. Pineville Tripolite facies isopach map (thickness <10 in red).

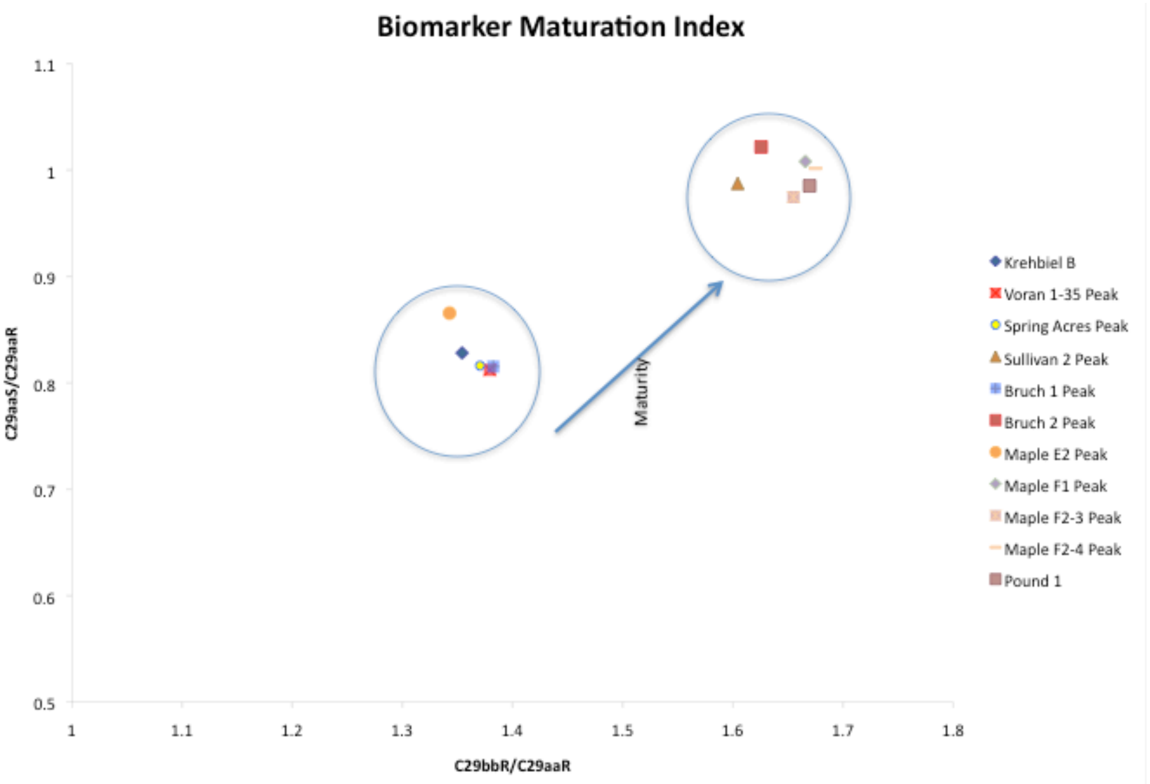


Figure 10. Biomarker Maturity Index with maturity groups circled.

5.2.3 Petrophysical Log Properties

Many of the down-hole properties of the Pineville Tripolite were from geophysical well log data. The most commonly used type of well logs in recognizing the Pineville tripolite were: neutron/density porosity, resistivity, spontaneous potential, gamma ray, bulk density and radiation-guard. From analysis of the porosity logs, it was ascertained that the Mississippian formation is a very dense tripolitic chert with low permeability values of 5-10 mD. The porosity logs were set to limestone calibration, which proved common and useful in evaluating density and identifying the formation boundary. The spontaneous potential logs demonstrated a common leftward, negative deflection, indicative of highly saline formation waters and porosity. From resistivity logs it is easily observed that the formation is very water saturated and low very low resistance. Gamma ray logs were useful to demark the boundary between the low-radioactive Mississippian and the highly radioactive Pennsylvanian.

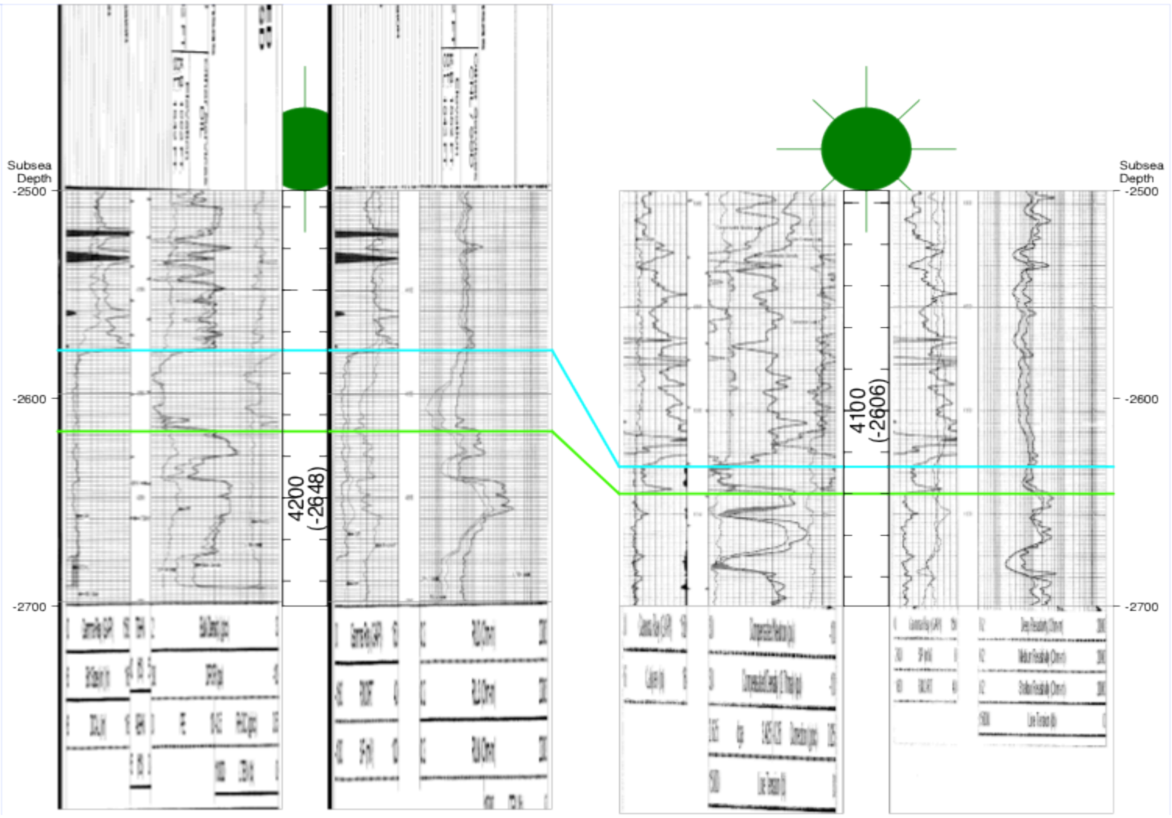


Figure 11. Petrophysical logs showing Pineville Tripolite characteristics. Pineville top (blue), bottom (green).

Chapter 6 –

6.0 Discussion

The Spivey-Grabs-Basil Oil field is a highly productive oil field in south-central Kansas, and has created many fortunes. However, pitfalls are common when drilling in this field, where production is lacking or even reservoir rock is nearly non-existent. These occurrences lead the prospectors to suspect the field is highly compartmentalized. This investigation is more proof that the use of biomarkers in oils can be used to locate compartments. The use of biomarkers also can impart knowledge about oil's source and maturity and any alterations occurring upon the oil. Biomarker evidence indicates that the field has received very slight to slight biodegradation or 1and 2 based upon Wenger's Biomarker Biodegradation Scale (Table 3). The shear presence of methylphenanthrenes, and little alterations to the n-alkylcyclohexanes in figure 21 indicates this point.

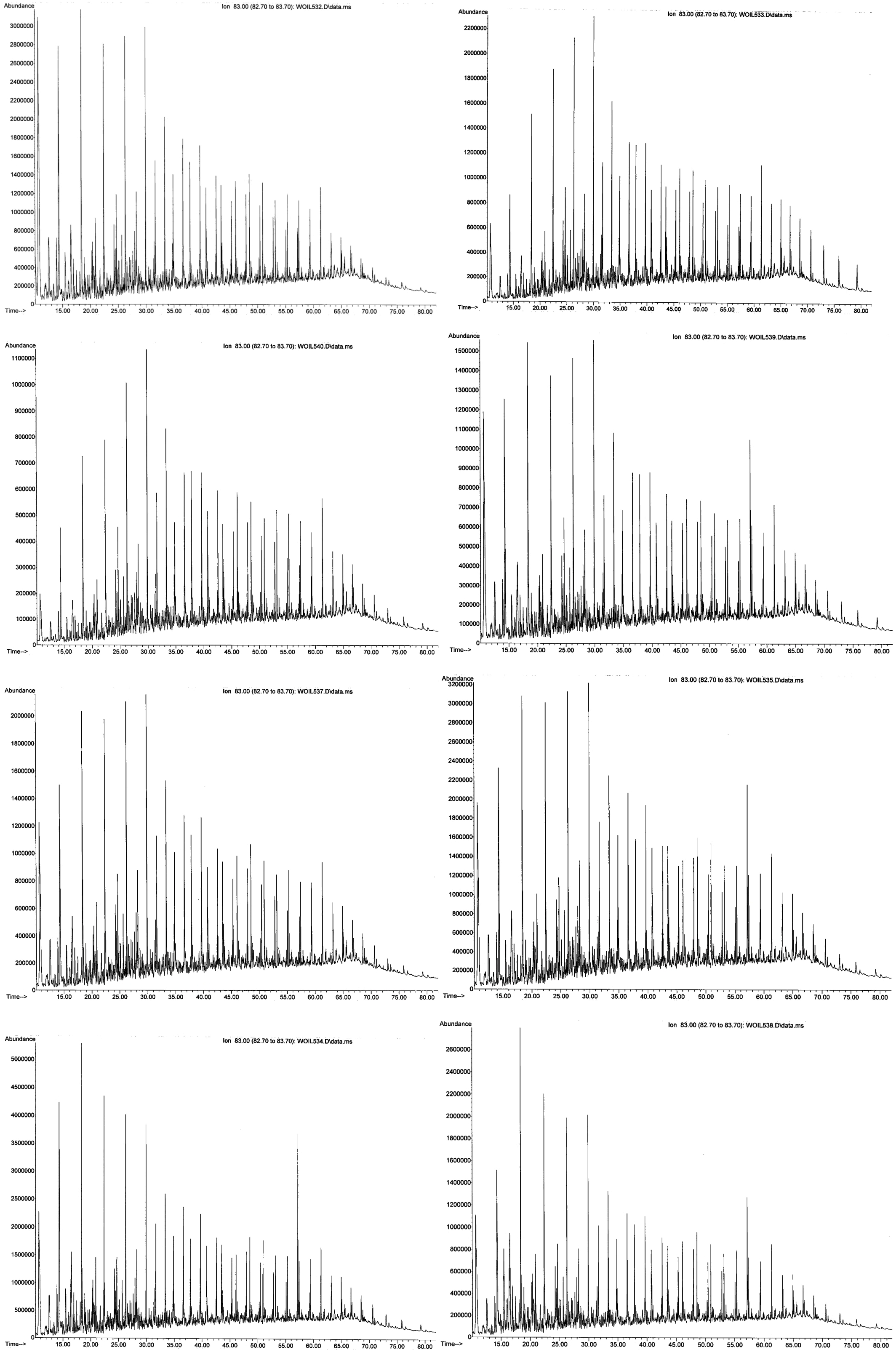


Figure 12. M/Z 83 n-alkylcyclohexane chromatograms (clockwise): Pound 1, Krehbiel B1, Maple E2, Spring Acres 1, Bruch 2, Maple F1, Bruch 1, and Voran 1-35.

Biomarkers evidence confirms the oil was generated out of a the same marine carbonate-rich shale source rock as seen in figures 22 and 24, and that was deposited in near suboxic waters as observed in figure 23, from Type II or II-III kerogen. It is from shale sources that tricyclic C_{24} terpanes are preserved and created. Because carbonate source rocks are the leading producer of C_{22} tricyclic terpanes, this biomarker is very useful to identify source as observed in figure 22. However, many of the tricyclic terpanes source one another from cleaving of lower number terpanes, as brought about by maturity making them more useful in maturity analysis than in source-type evaluation. Depositional environment plays a major role in the preservation of several biomarkers: n-C_{17}, n-C_{18}, pristane and phytane. As seen in figure 23, the more reducing an environment, the more likely it is for the n-C_{17} and n-C_{18} to be deposited and maintained. In addition, the more reducing the area, the more likely it is for phytol to be converted into Ph and vice versa for oxidizing environments. Not only can the Eh value influence the biomarkers, but so to can the maturity and biodegradation. Figure 23 indicates that the increasing biodegradation will boost Pr and Ph becomes in the rock while increasing maturities will lower these biomarkers.

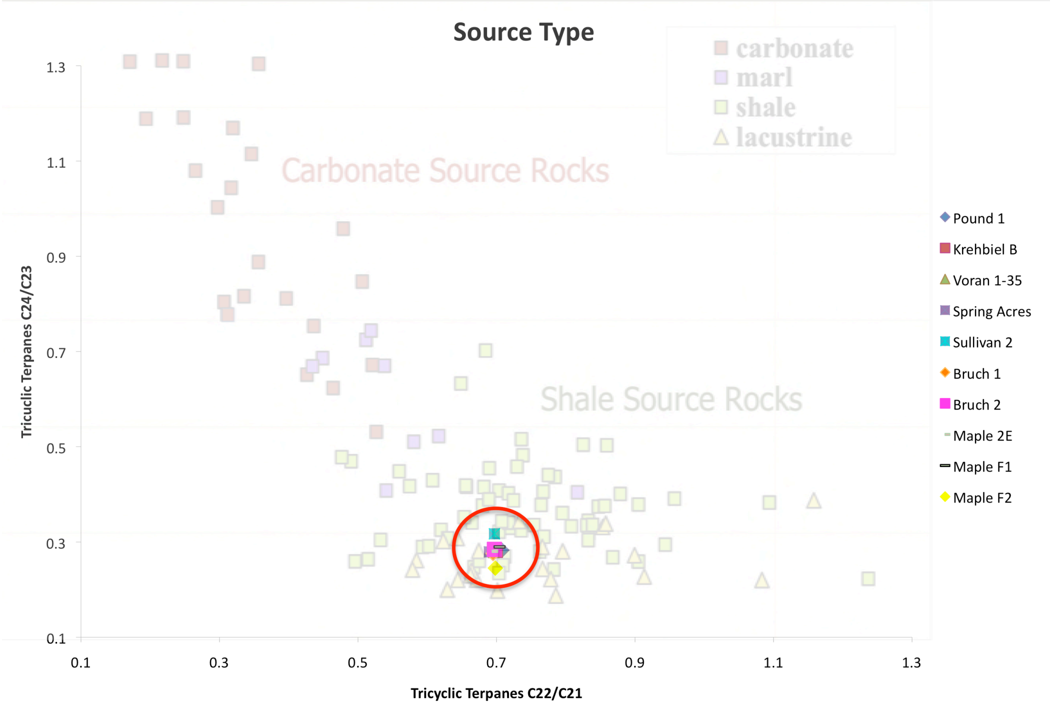


Figure 13. Oil source rock type with research samples circled. (modified from Ferworn et al., 2003)

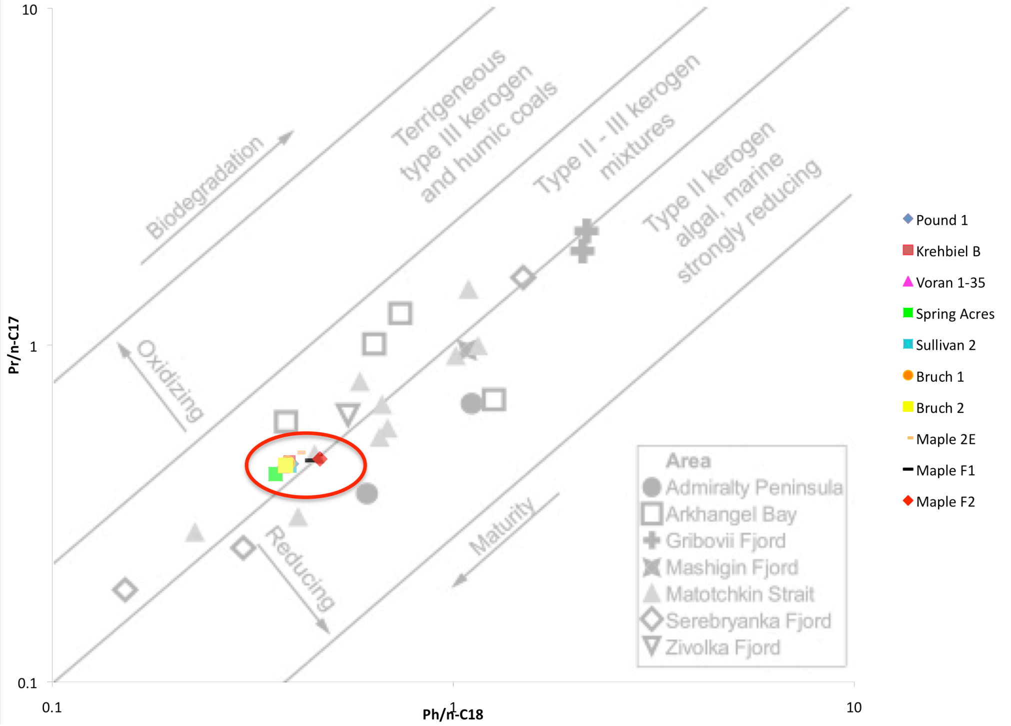


Figure 14. Oil source rock depositional environment, research samples colored (modified from van Koeverden et al., 2010).

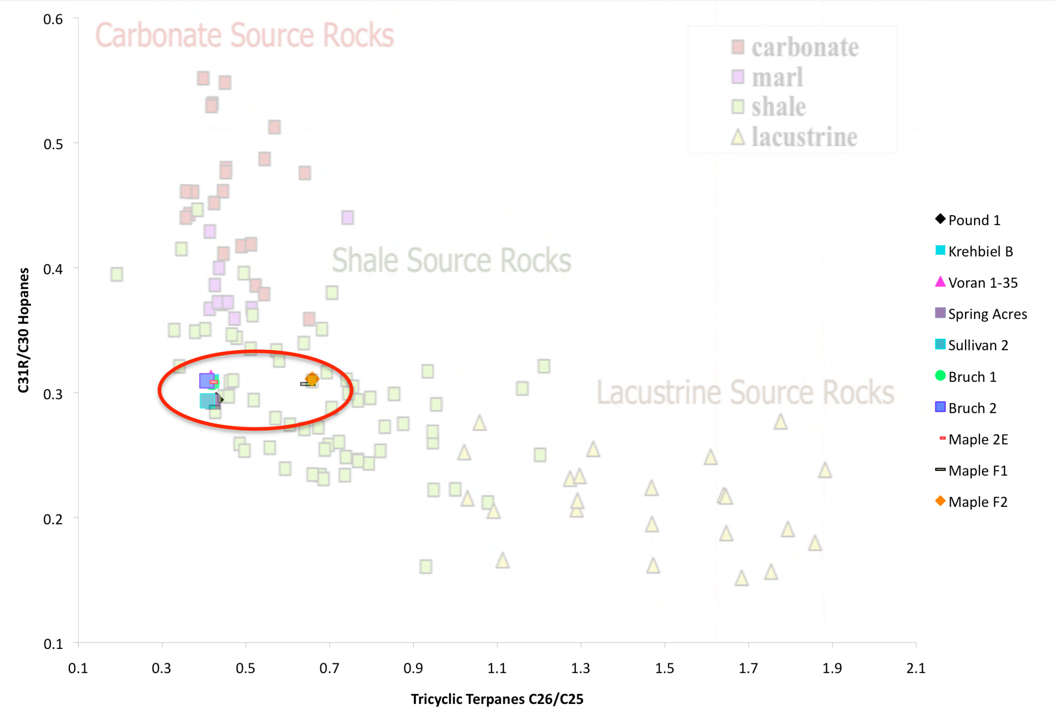


Figure 15. Oil Source rock, research samples circled. (modified from Ferworn et al., 2003)

Based upon thermal maturity biomarkers, two distinct maturities are encountered in the study area: peak and near peak based upon the C_{29} hopane, C_{32} steranes and trisnorhopane (Ts) isomers . Figure 25 highlights this statement about segregation of thermal maturities. It is along with evidence from other maturity parameters in figure 26 that the source is nearly entering the peak oil generation window, and shows age segregation too. This figure shows that the oil source has not quite entered into the peak oil window, where both oil and gas are produced. However, figure 27 illustrates that the source is not at the peak oil window for the C_{29} S&R stereoisomers, but the αα&ββ biomarker isomers are at peak oil window. Figure 27 also shows from the C_{32} sterane isomers and C_{33} hopane isomers that the oil source reached the peak oil window, allowing for the production of oil & gas.

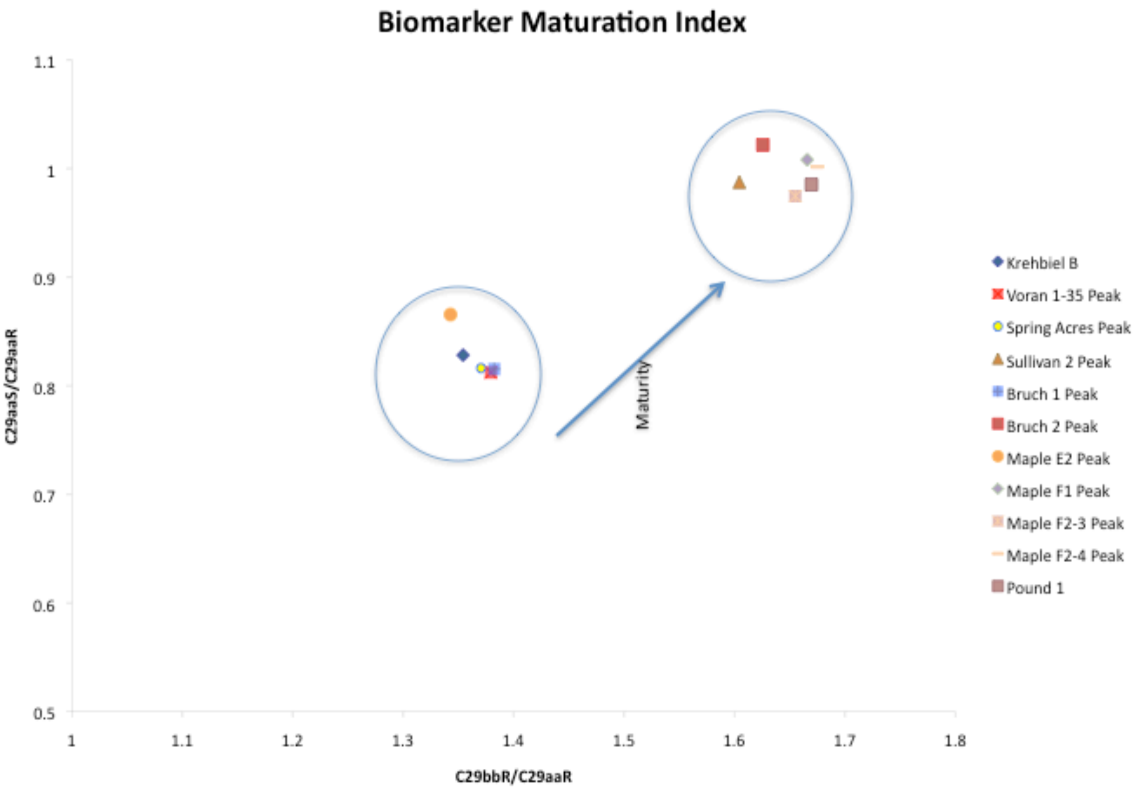


Figure 25. Biomarker Maturation Index

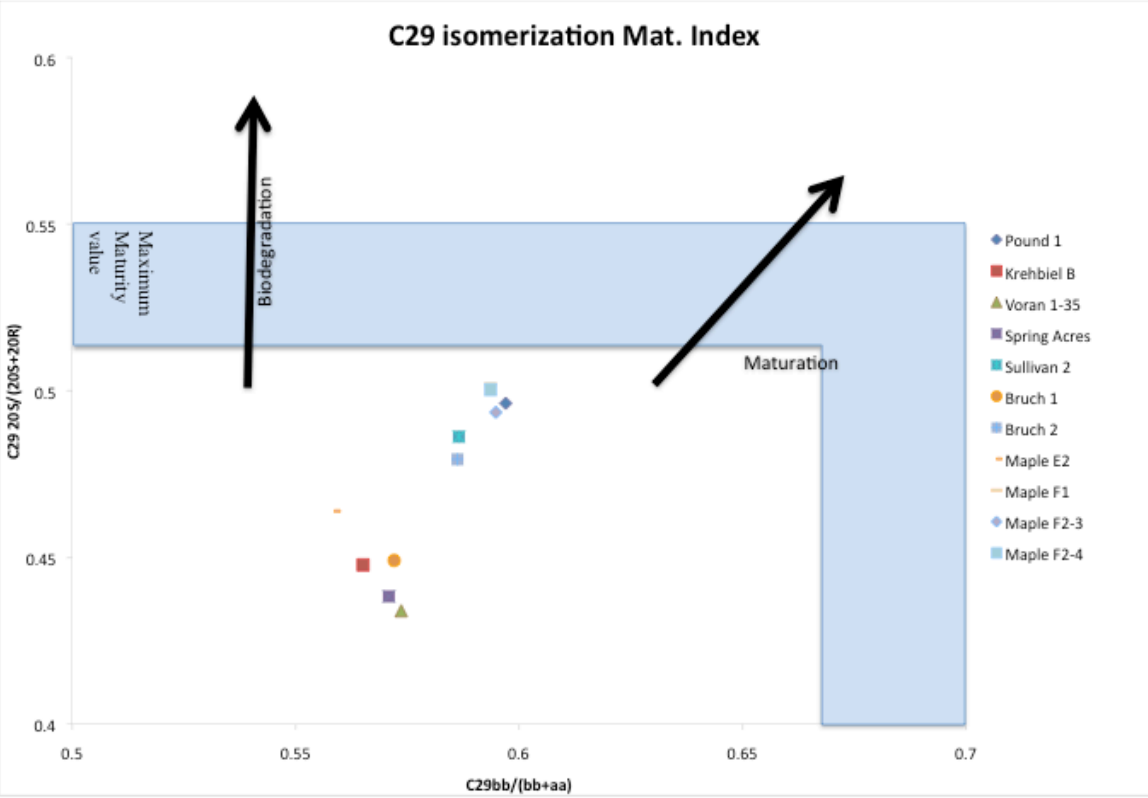


Figure 26. C_{29} isomerization Maturity Index (modified from Peters et al., 2005).

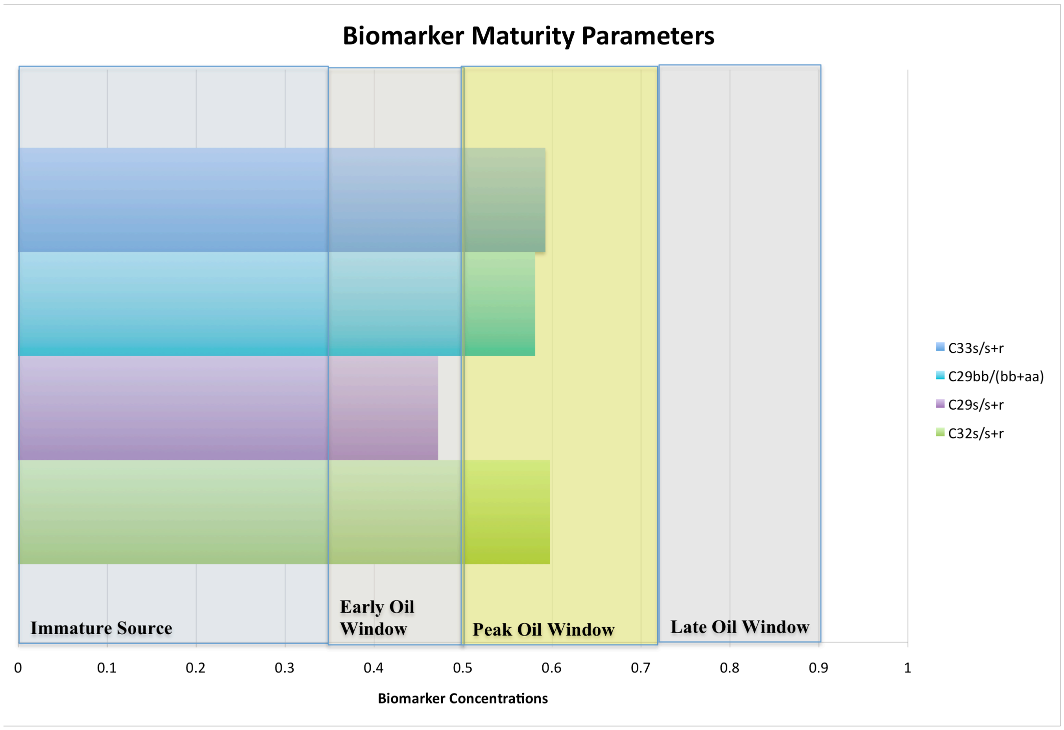


Figure 27. Biomarker Maturation Index Parameters (modified from Peters et al., 2005)

It was also observed that three and possibly four compartments were delineated in figure 28. One area is in the southwestern quarter of section 35 encompassing the Voran 1-35 well that has both lower field maturity and a reservoir thin (red) northeast of the well when compared to its surrounding wells. The second compartment appears with the Sullivan 2 and Pound 1 wells, both in a isopach thick area, not divided by any thin (red) and having same thermal maturities. The third compartment begins northeast of Sullivan 2 in section 26 at well Krehbiel B1, with biomarker thermal data supporting that the Maple E2 may also be in the same compartment. Biomarker data pertaining to the Maple F1 and F2, along with the Bruch 2 indicates another compartment, but isopach data shows no reservoir thin. A forth compartment appears based upon maturity data when discussing wells Spring Acres 1 and Bruch 1. Again, these well do not appear to be separated by any thin from other wells within the Pineville Tripolite facies.

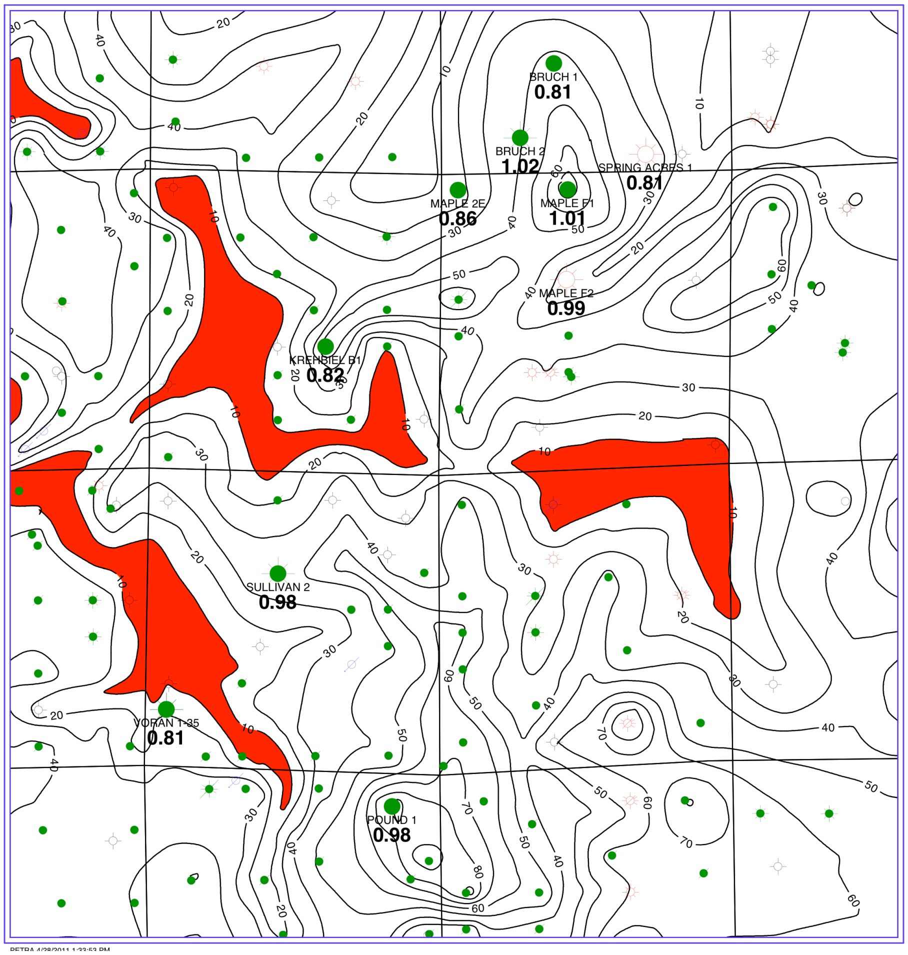


Figure 28. Pineville Tripolite facies isopach map with maturity values below each well (reservoir thins/pinch outs in red).

After investigating various publications on the Pineville Tripolite, this oil separation and maturity heterogeneity may be due to the fact that the field filled at different times from the same source rock. Oil from a mature source filled the areas of the field and ceased, allowing for the source rock to mature more. Faulting occurred again, filling newer compartments with more mature oils. This faulting most likely occurred before and during Cherokee time, where slight thickness variations do occur between the Pineville Tripolite facies and the Cherokee formation.

Philp (1997), investigated the Anadarko Basin and its possible source rocks, analyzing the Viola, Springer, Morrow, Woodford and Mississippian rocks for source potential. When comparing statistical data between this investigation and Philp's, some parallels begin to appear. For instance, The Viola formation is a limestone having large amounts of carbonate in its lithology. The Viola formation has very high amounts of C_{30} hopanes, Tm>Ts, and fairly abundant C_{27} diasterane counts. In addition, source dependent biomarkers $C_{27\text{-}29}$ meet the same percentages amounts for this specific rock. This rock formation is present in the study area, having been penetrated by drilling rigs, allowing this rock to be analyzed for future studies. In addition, the Woodford shale should not be ruled out as a possible source rock due to its carbonate-rich qualities and comparable attributes. However, Philp's samples were taken from locations far from this study's area, and therefore analysis of these formations in the Spivey-Grabs-Basil area may show considerable differences.

Chapter 7-

7.0 Conclusion

This investigation emphasizes the melding of well-log analysis, subsurface mapping and oil geochemistry in identifying compartments. The Pineville Tripolite is a highly porous chert facies that came from meteoric alteration. Indication of compartments based upon several biomarker values and an isopach map appear in the area of study. From quantitative analysis of the biomarkers, it is observed that the thermal maturity of the source rock is into the peak oil window from C_{32} and C_{33} hopane isomers (0.6). C29 sterane isomer values indicate that the maturity of the source is reaching early to peak oil window whose maximum values are reached at the early (0.47) and peak oil windows (0.58). The Biomarker Maturation Index shows two highly clustered thermal maturities in this field with one cluster slightly less mature than the other as does the C29 isomers. Observations of the n-alkane and isoprenoid values indicate that the oil source is highly matured.

Pristane/phytane ratio values reached 1.16, indicating a depositional environment was a suboxic, showing increased maturities from initial source deposition. The prominent source rock type is rather mixed, but the conclusion is that it is carbonate-rich shale, showing that the oil biomarkers fall into both the shale and carbonate parameters. As observed from the Biomarker Maturation Index, there appears to be two distinct source rock maturities for the area of study: a mature and less mature source. As illustrated by the BMI chart and well location map, several areas within the field have distinct differences in maturity. Peters et al. (2003) stated that while a reservoir fills, if mixing of the oils is not allowed, this is indicative of compartments and can create separation between the oil types. If separation does occur between different maturities, the less mature oil is assumed to have migrated further than the more mature oil. This fact of segregation is observed in the study area, with little biodegradation may indicate that this field filled at different times from the same source rock. The other biomarker quantities show little indication of compartments, but indicate that all oils are from the same source. Isopach maps indicate separation of different areas where the maturities are also separated out. The Voran 1-35 well has a Pineville Tripolite formation thin northeast of its location and has a different maturity values from the Sullivan 2 and Pound 1 wells, the closest neighboring wells. Sullivan 2 is also different of maturity from the Krehbiel 1 well, located north of Sullivan 2. Between these two wells is an isopach thin, possibly separating the two. In sections 25 and 24, there are distinct maturity variations, but little evidence from the isopach of lithological barriers. The Bruch 2, and Maple F1 and F2 wells show strong maturity correlation, but few similarities to the Bruch 1, Maple E2 and Spring Acres wells. None of these wells are indicated to be separate from each other by a barrier, yet there are differences between them.

Based upon the evidence and interpretation, the Spivey-Grabs-Basil oil field is compartmentalized pertaining to the Pineville Tripolite facies. Isopach data and biomarker analysis shows evidence that the compartments can be identified based upon the thermal maturity biomarkers from different filling times.

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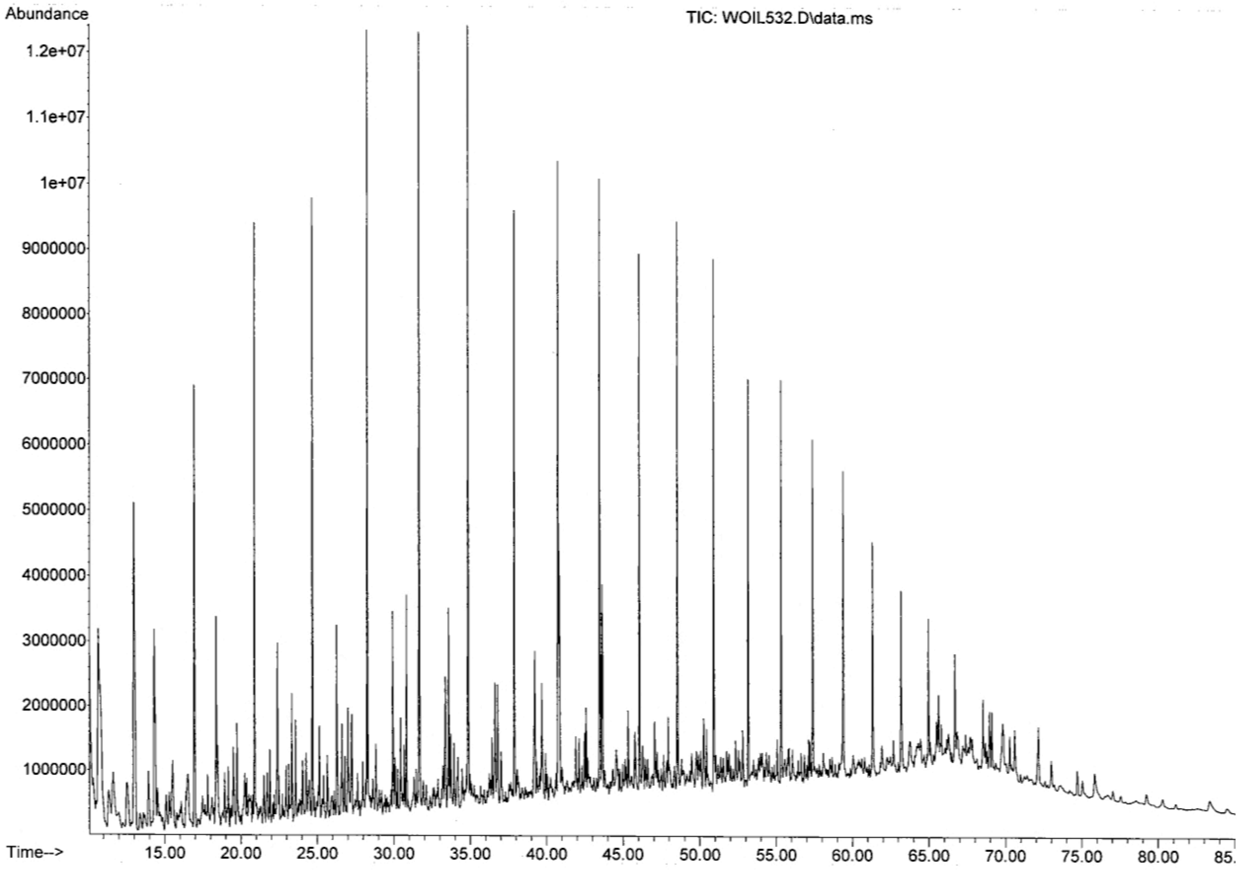
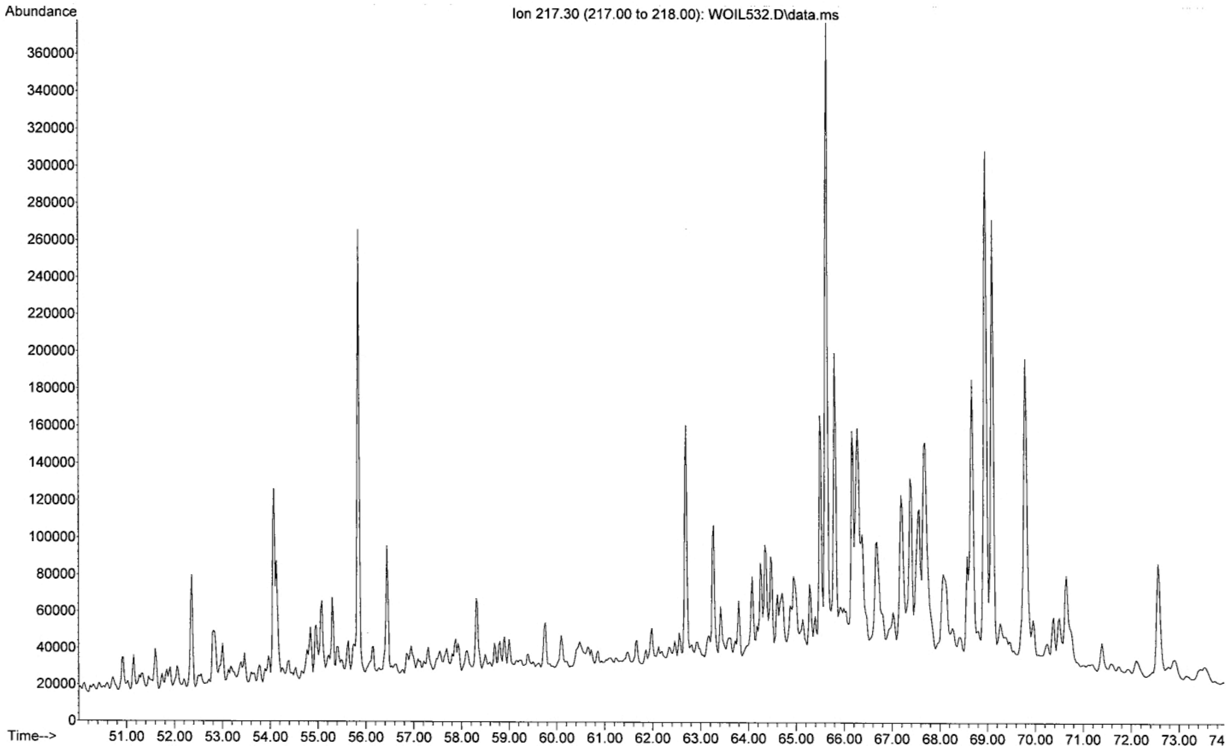
Appendix A - Gas Chromatograms

Each of the following are four gas chromatograms of each well sampled and analyzed. The first chromatogram is the TIC or whole oil, second is the m/z 217 or sterane chromatogram, third is the m/z 191 or terpane chromatogram and finally, the m/z 83 or n-alkylcyclohexane chromatogram.

Pound 1 Gas Chromatograms


Abundance
TIC: WOIL532.D\data.ms
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
80.00
85.


Abundance
Ion 217.30 (217.00 to 218.00): WOIL532.D\data.ms
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Time-->
51.00
52.00
53.00
54.00
55.00
56.00
57.00
58.00
59.00
60.00
61.00
62.00
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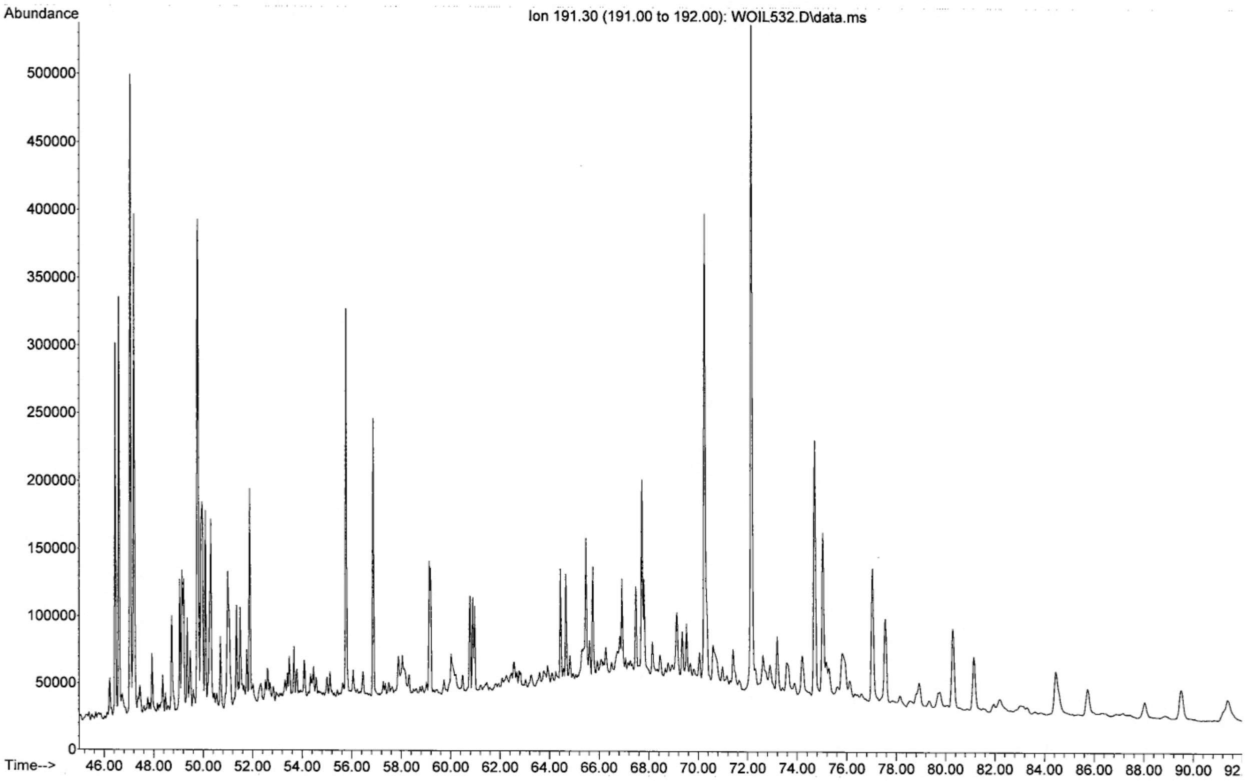
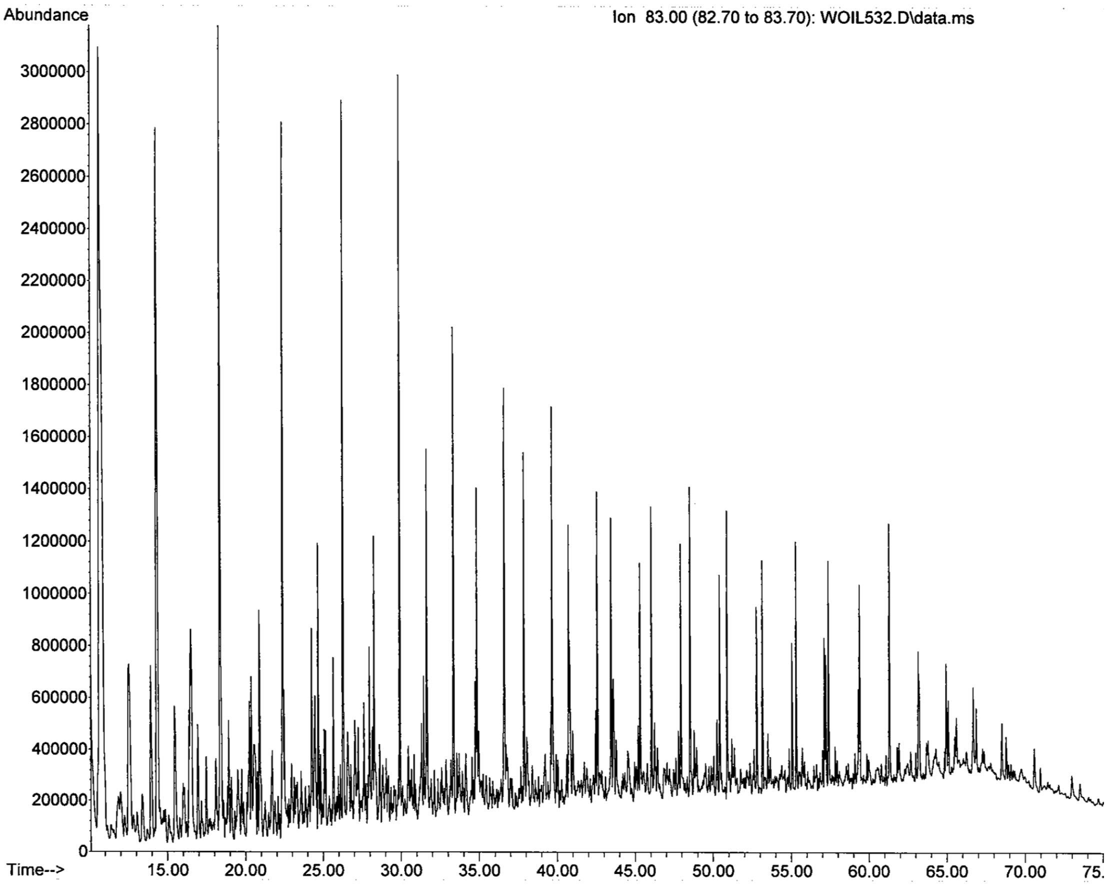
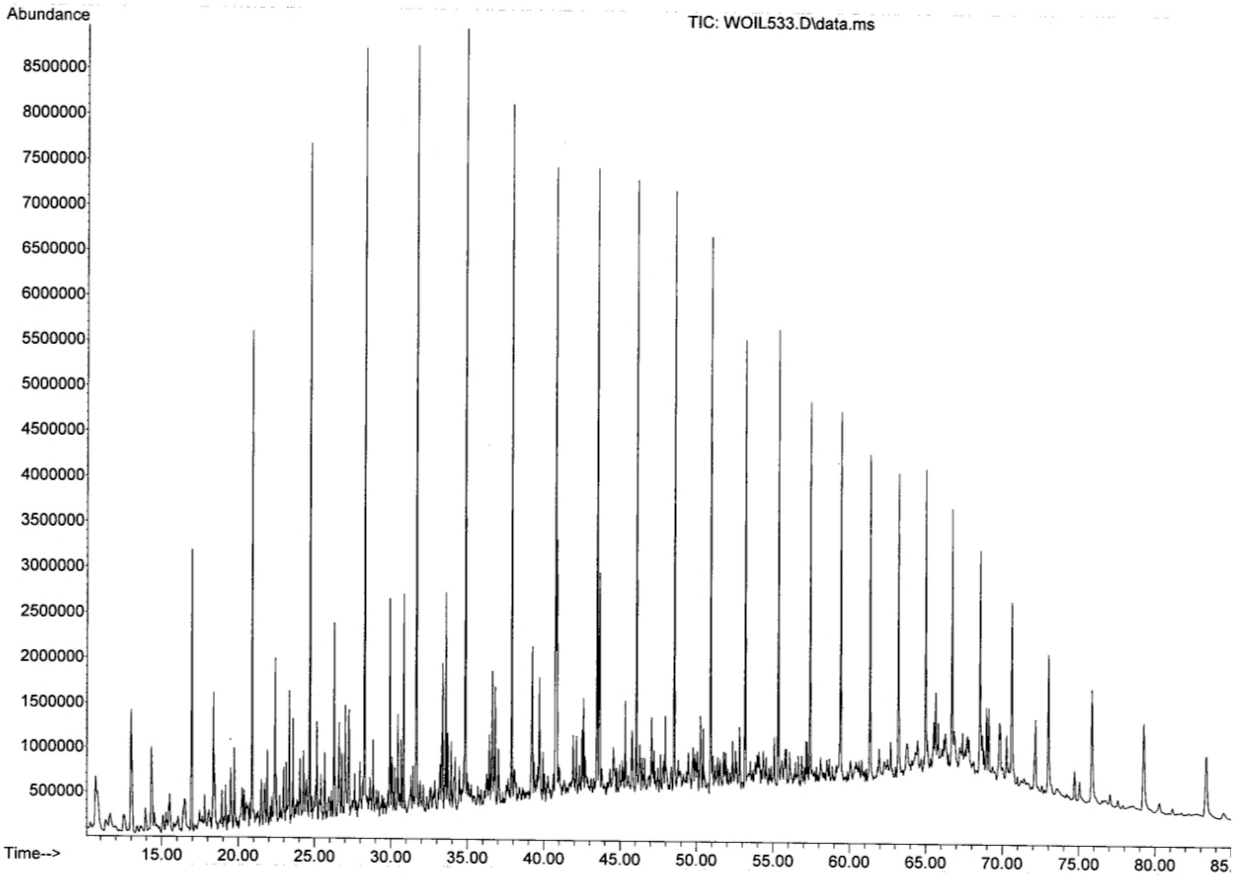
71.00
72.00
73.00
74


Abundance
Ion 191.30 (191.00 to 192.00): WOIL532.D\data.ms
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
Time-->
46.00 48.00 50.00 52.00 54.00 56.00 58.00 60.00 62.00 64.00 66.00 68.00 70.00 72.00 74.00 76.00 78.00 80.00 82.00 84.00 86.00 88.00 90.00 92


Abundance
Ion 83.00 (82.70 to 83.70): WOIL532.D\data.ms
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
Time-->
15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.

Krehbiel B1 Gas Chromatograms


Abundance
TIC: WOIL533.D\data.ms
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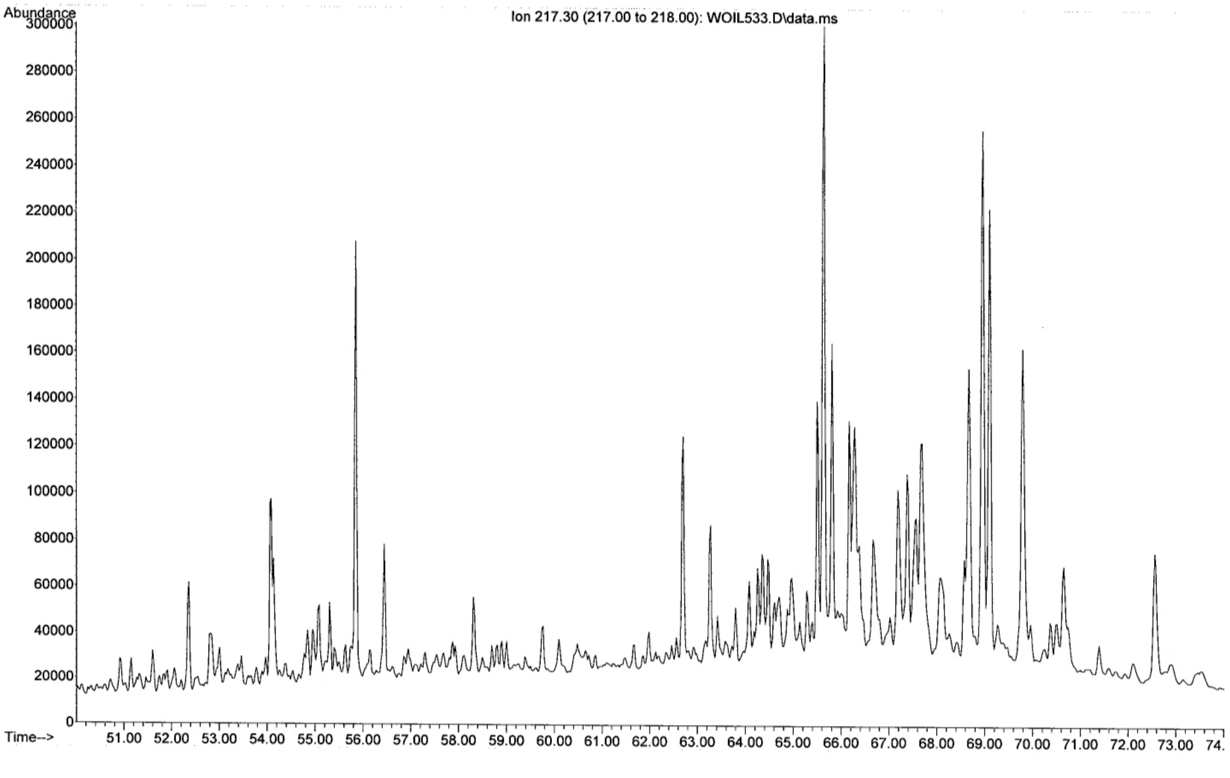
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
80.00
85.


Abundance
Ion 217.30 (217.00 to 218.00): WOIL533.D\data.ms
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
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20000
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Time-->
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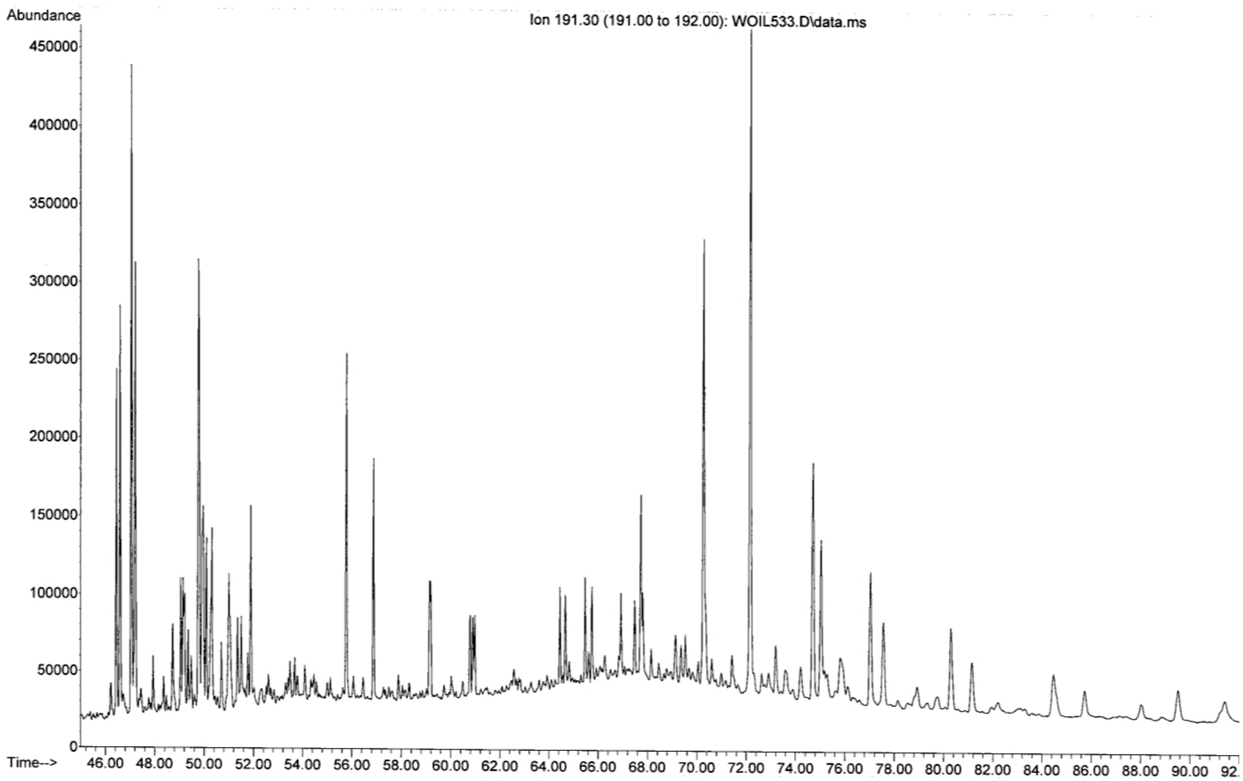
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48.00
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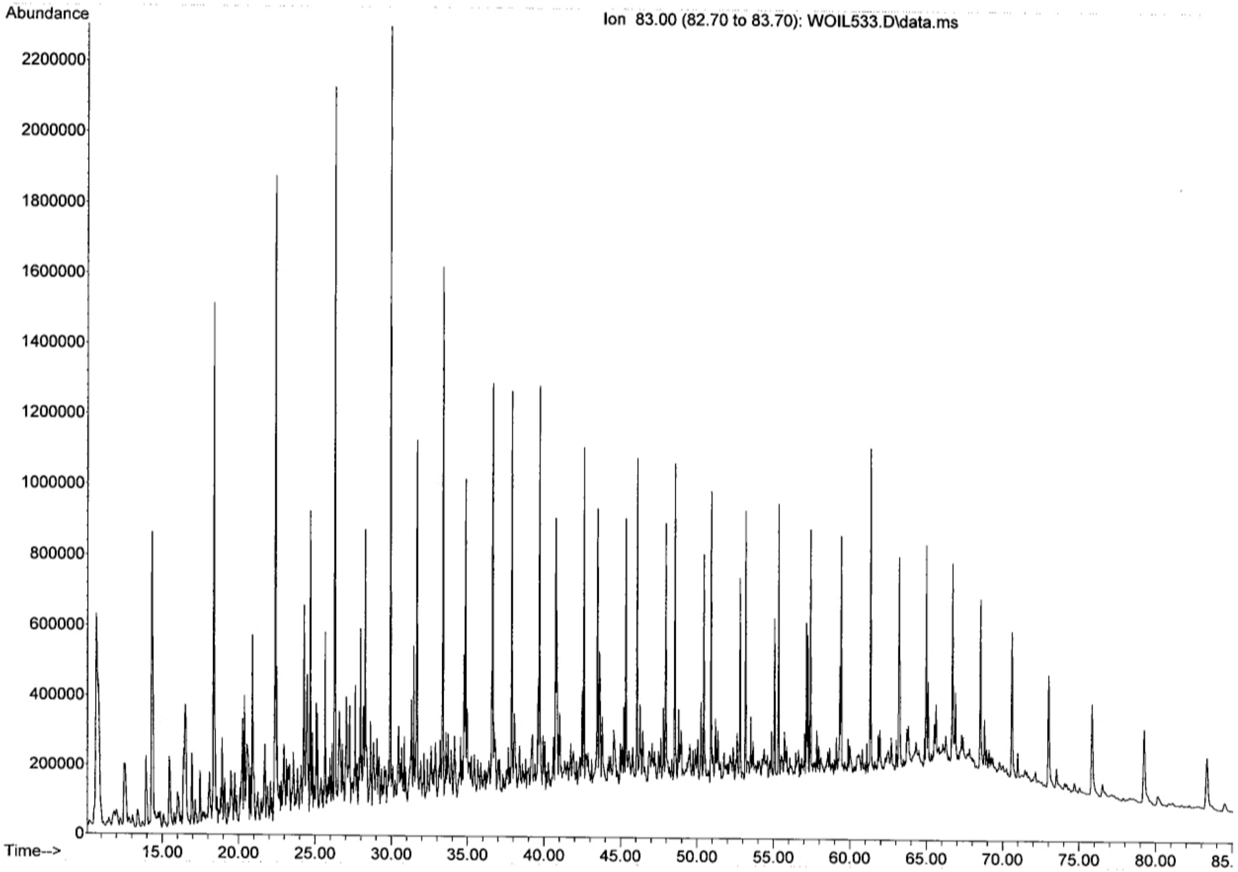
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Time-->
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20.00
25.00
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35.00
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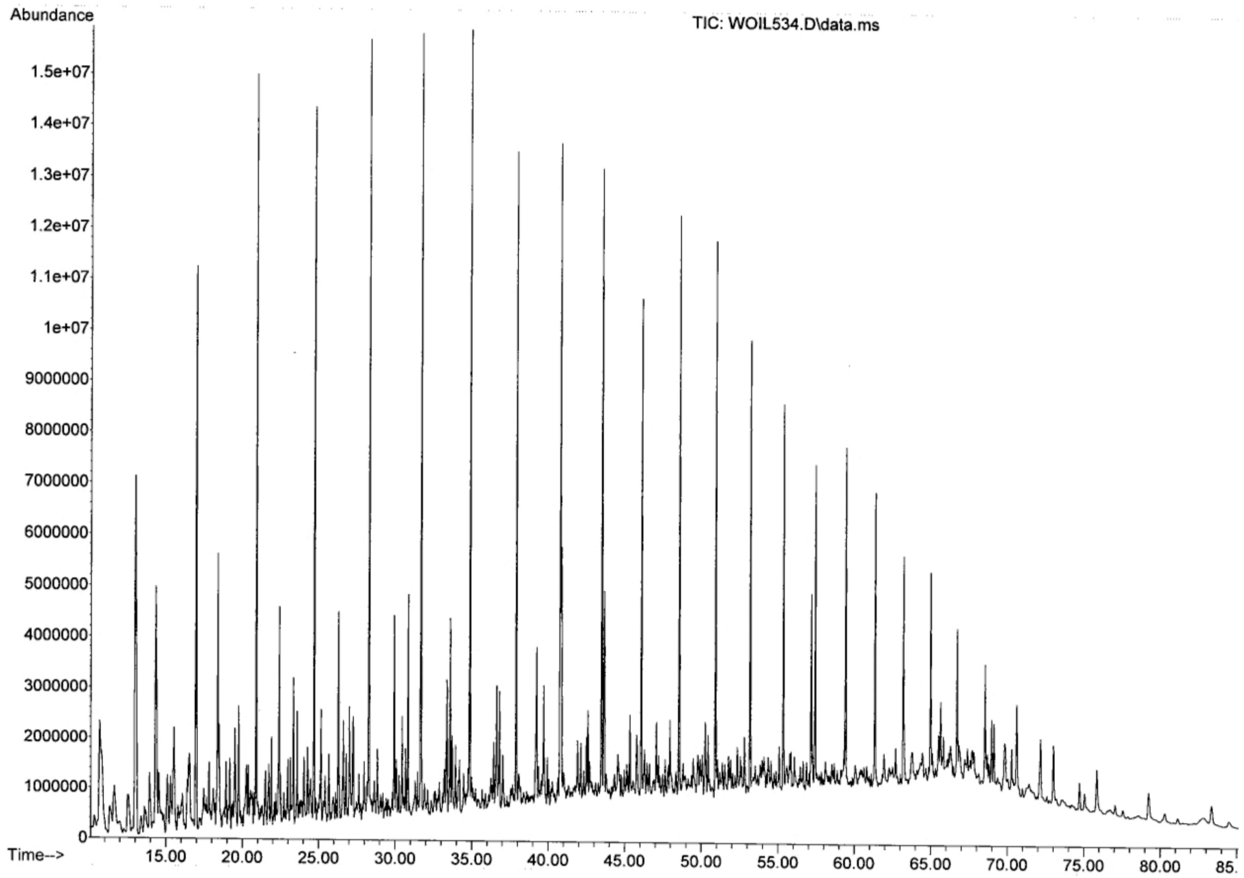
60.00
65.00
70.00
75.00
80.00
85.

Voran 1-35 Gas Chromatograms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1.1e+07
1e+07
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8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
Time-->
15.00
20.00
25.00
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65.00
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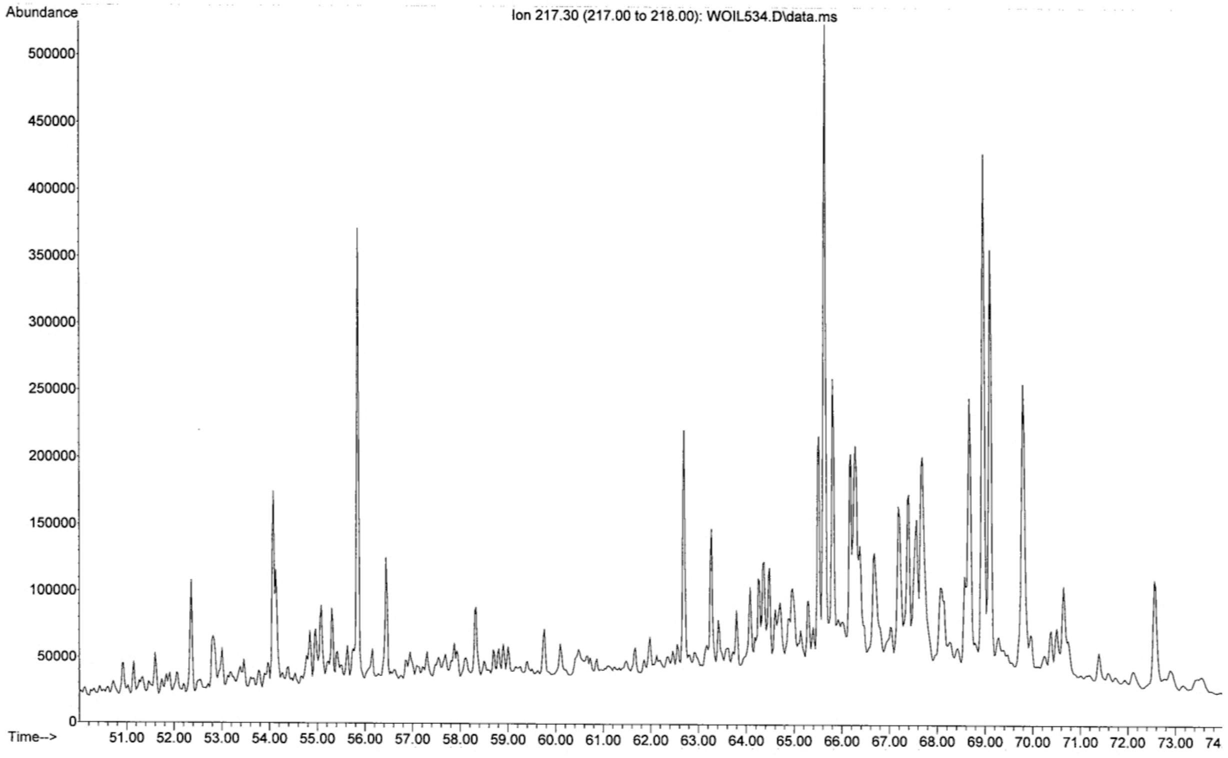
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300000
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200000
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100000
50000
0
Time-->
51.00
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54.00
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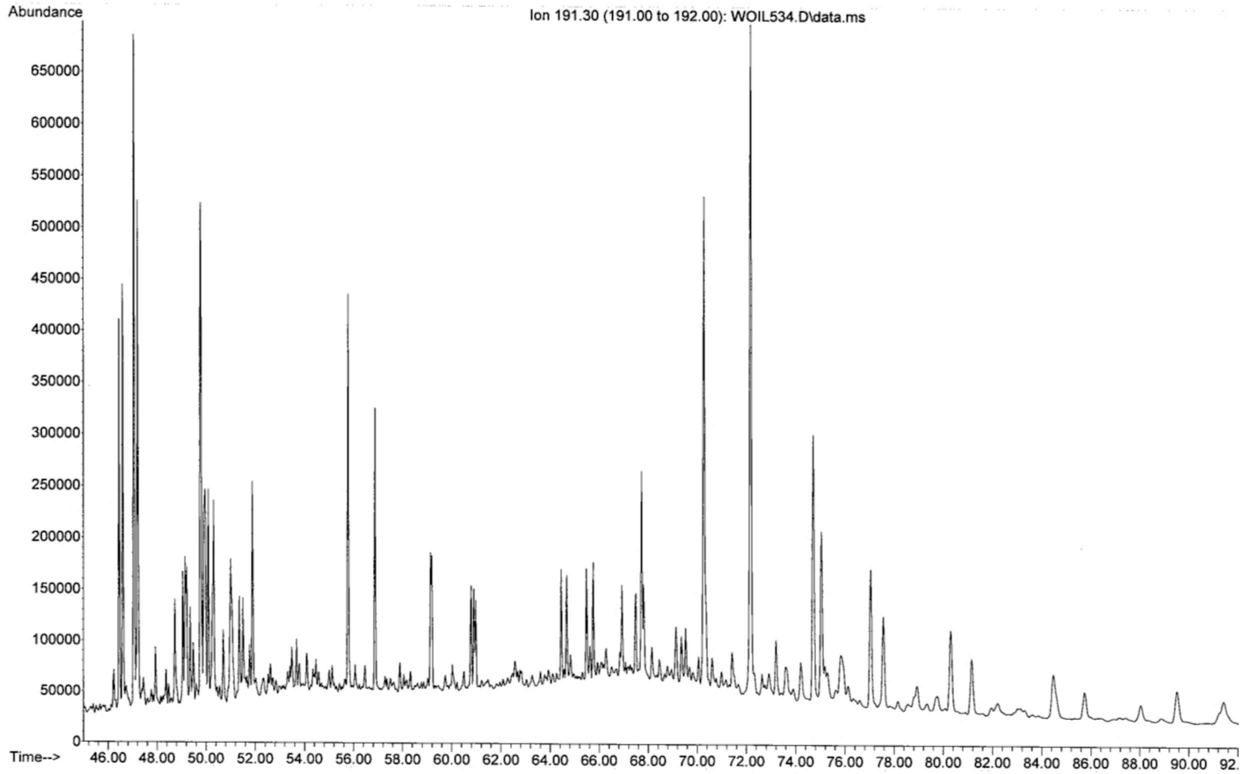
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50000
0
Time-->
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64.00
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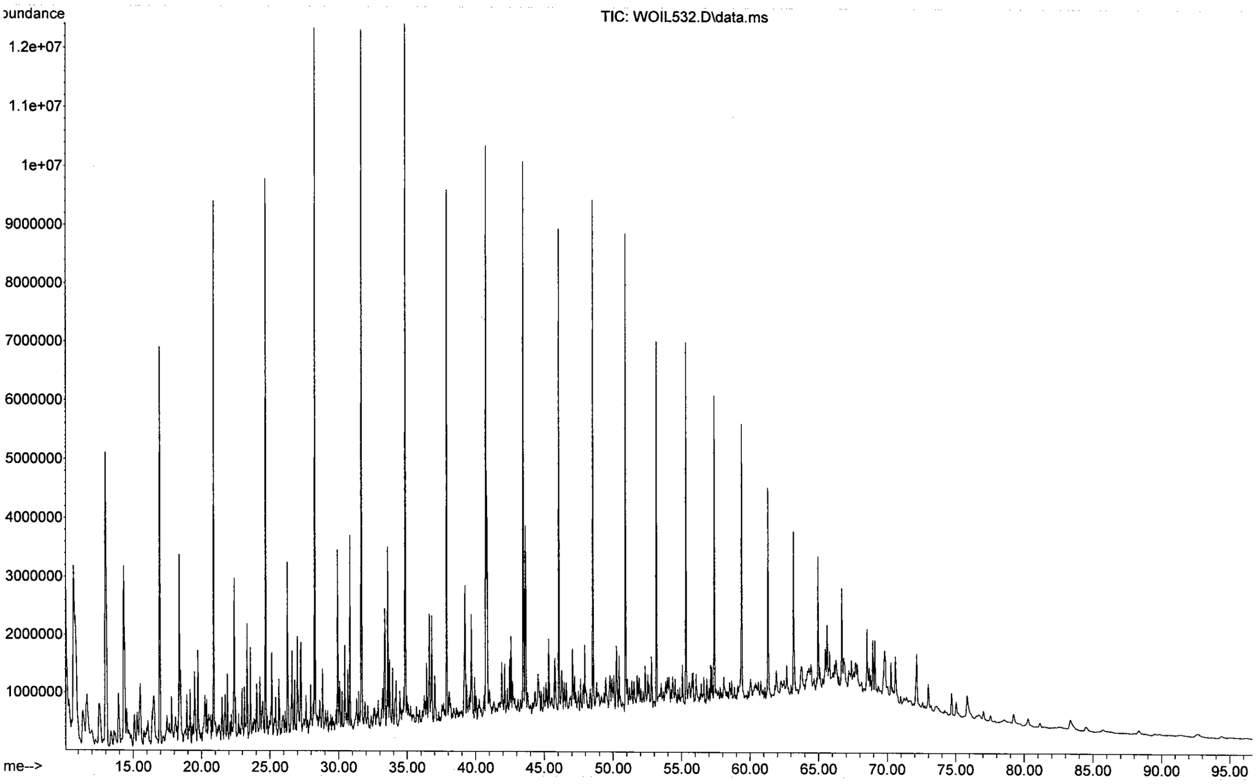
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25.00
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35.00
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45.00
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65.00
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80.00
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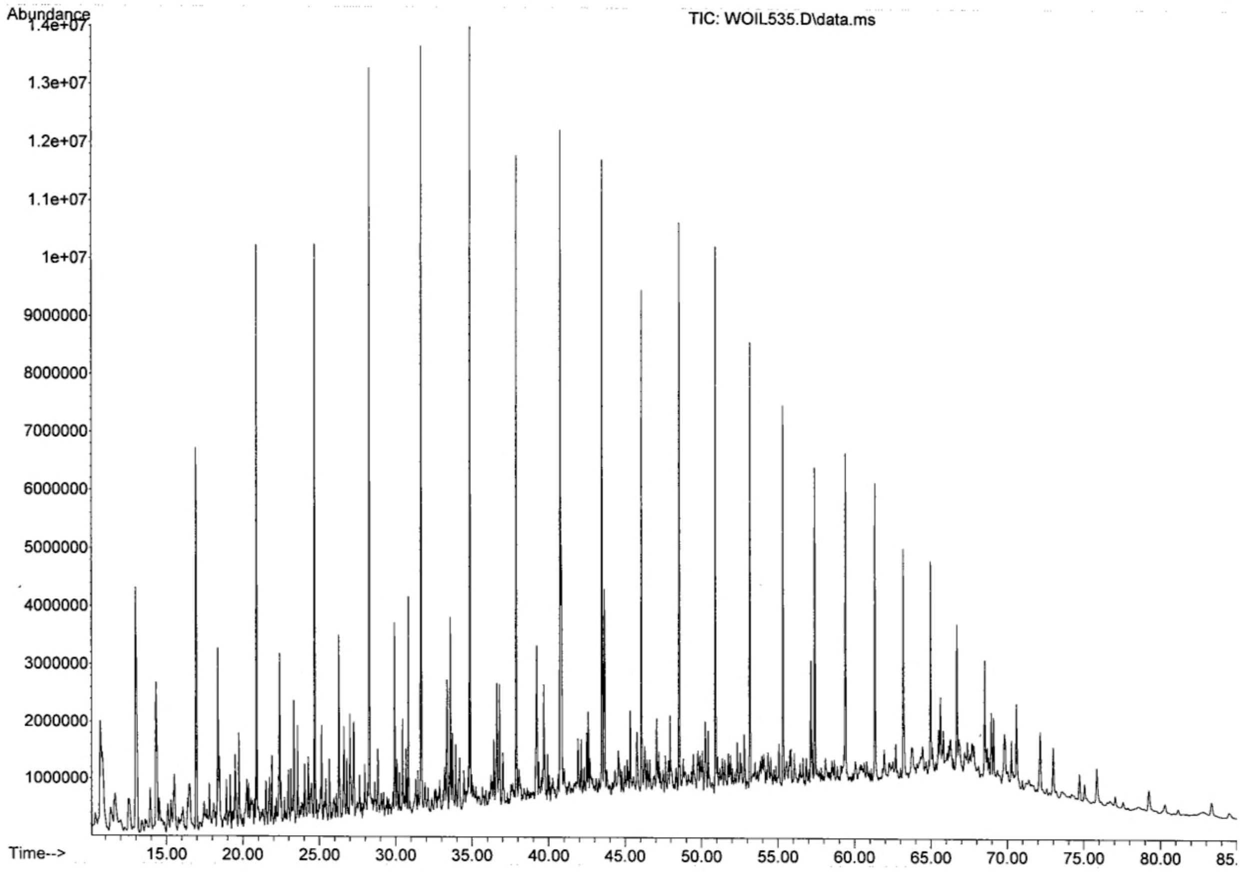
90.00
95.00

Spring Acres 1 Gas Chromatograms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1.2e+07
1.1e+07
1e+07
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8000000
7000000
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3000000
2000000
1000000
Time-->
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20.00
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45.00
50.00
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80.00
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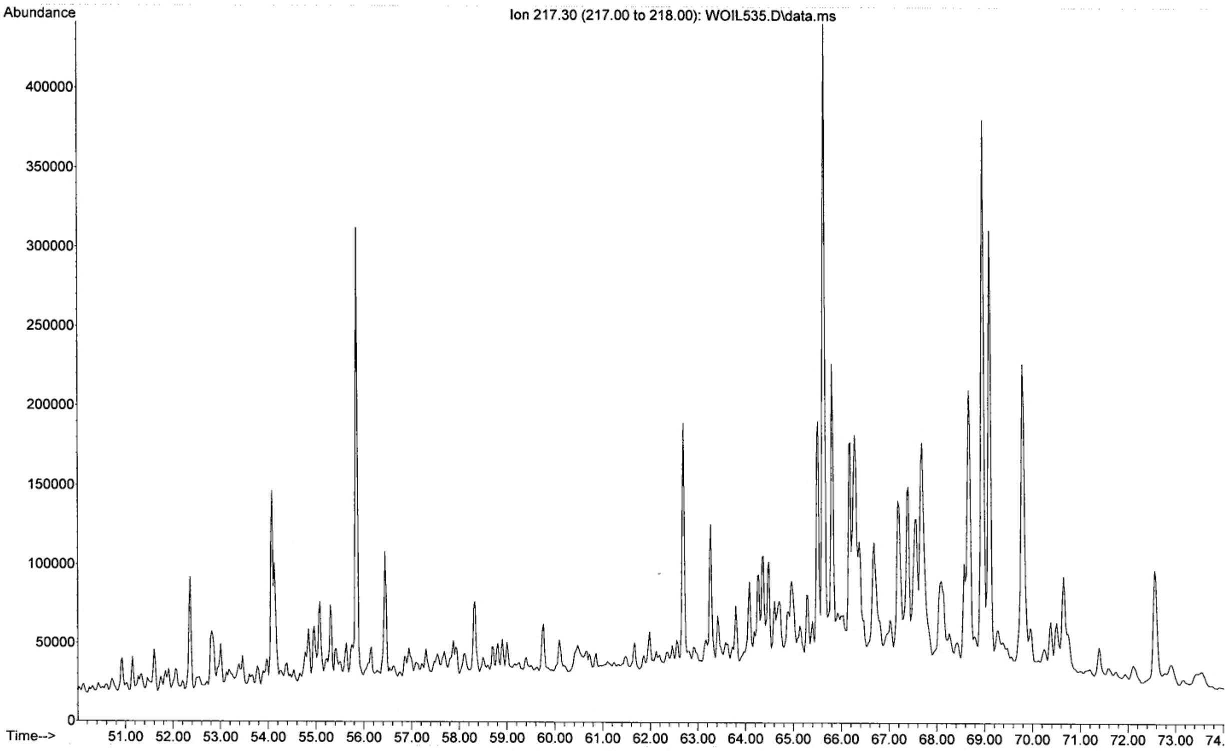
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Time-->
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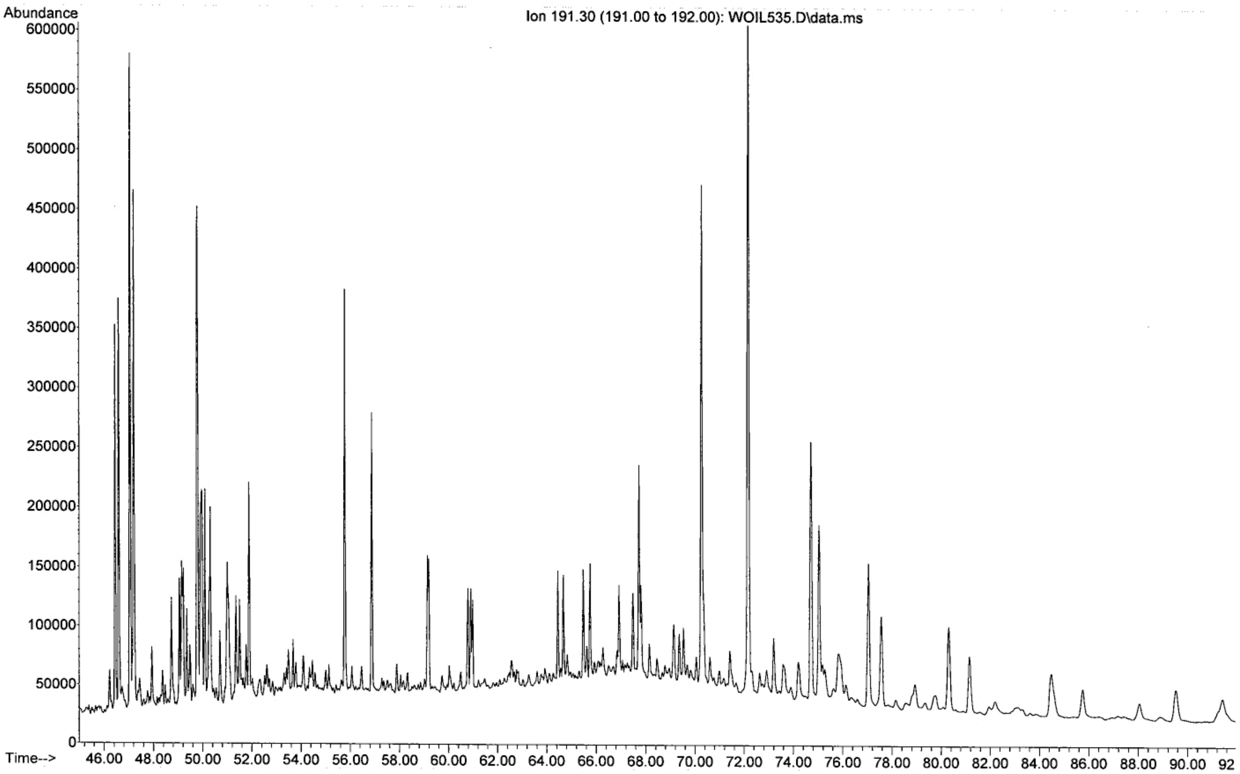
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100000
50000
0
Time-->
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56.00
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62.00
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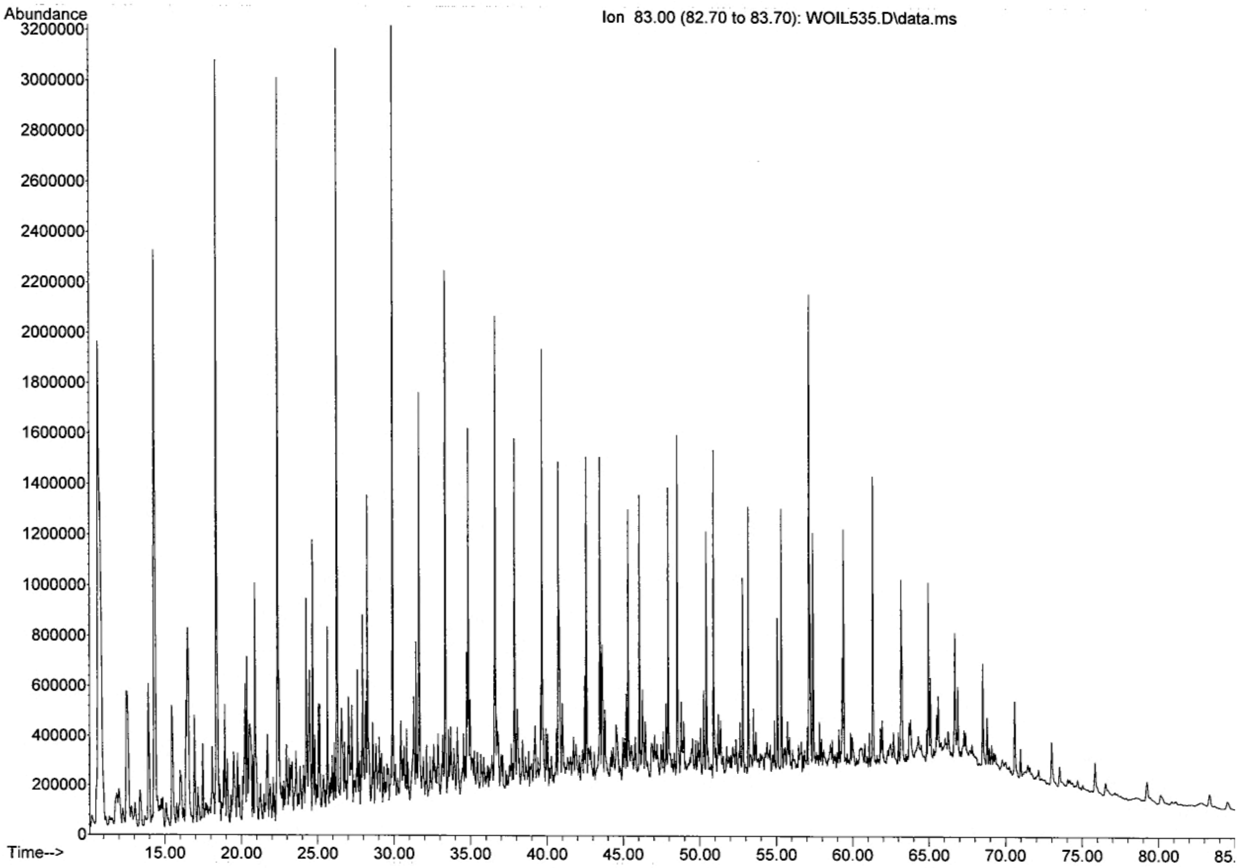
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1600000
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1200000
1000000
800000
600000
400000
200000
0
Time-->
15.00
20.00
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30.00
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50.00
55.00
60.00
65.00
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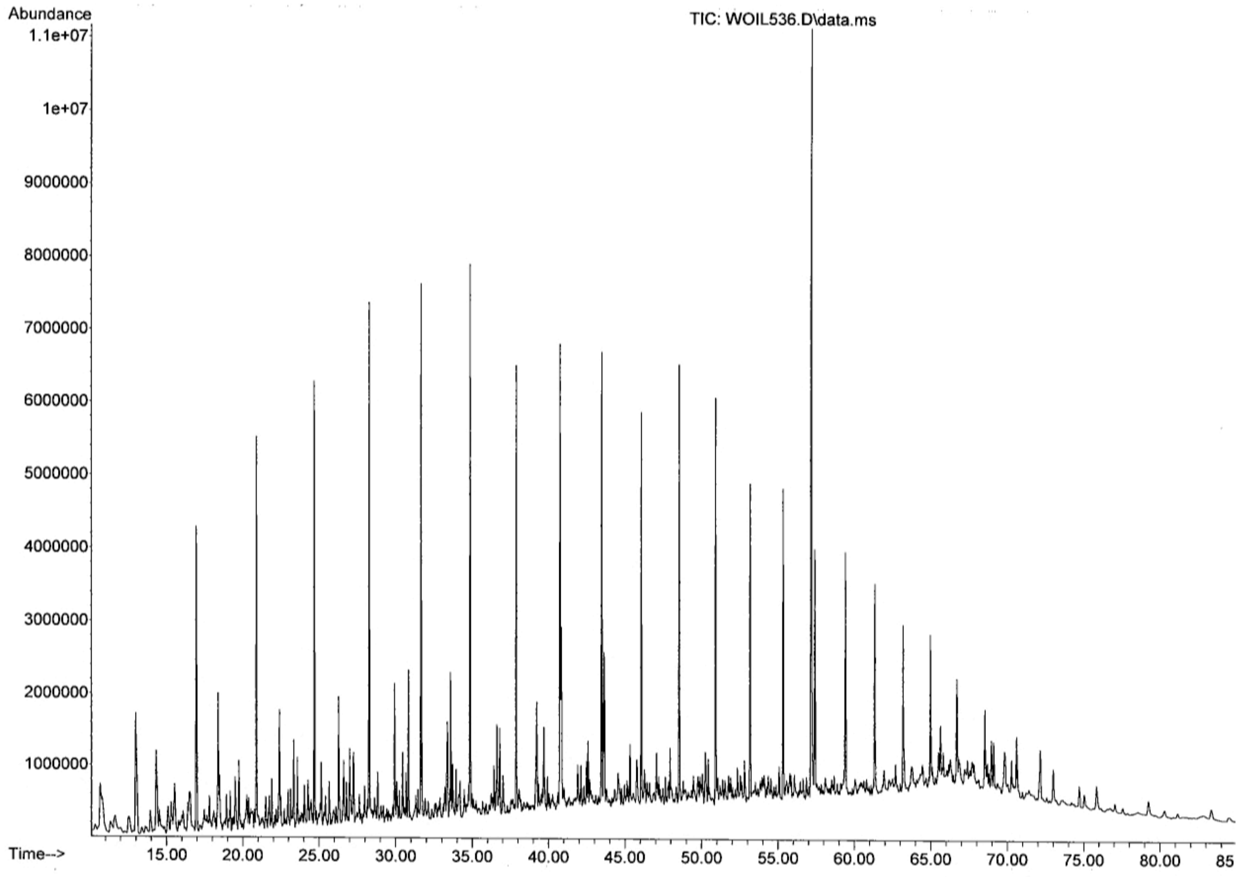
75.00
80.00
85.

Sullivan 2 Gas Chromatograms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5000000
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2000000
1000000
Time-->
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20.00
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65.00
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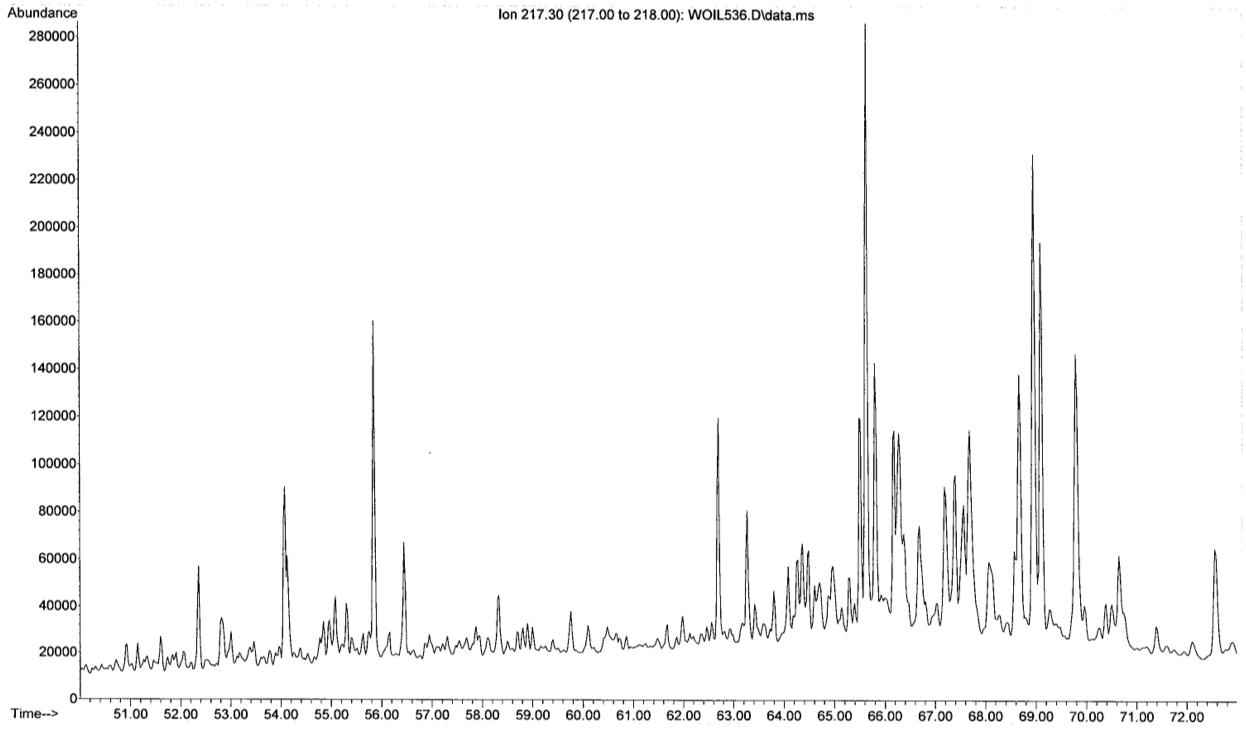
80.00
85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120000
100000
80000
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40000
20000
0
Time-->
51.00
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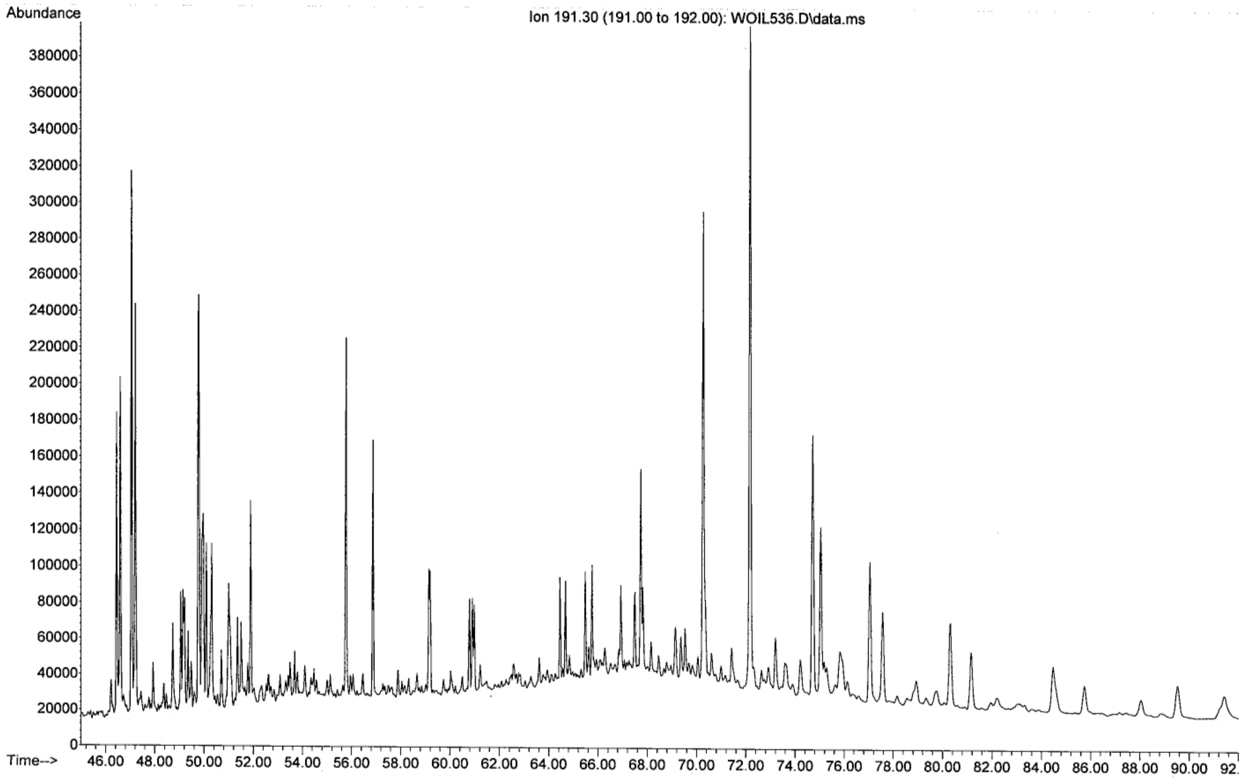
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20000
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Time-->
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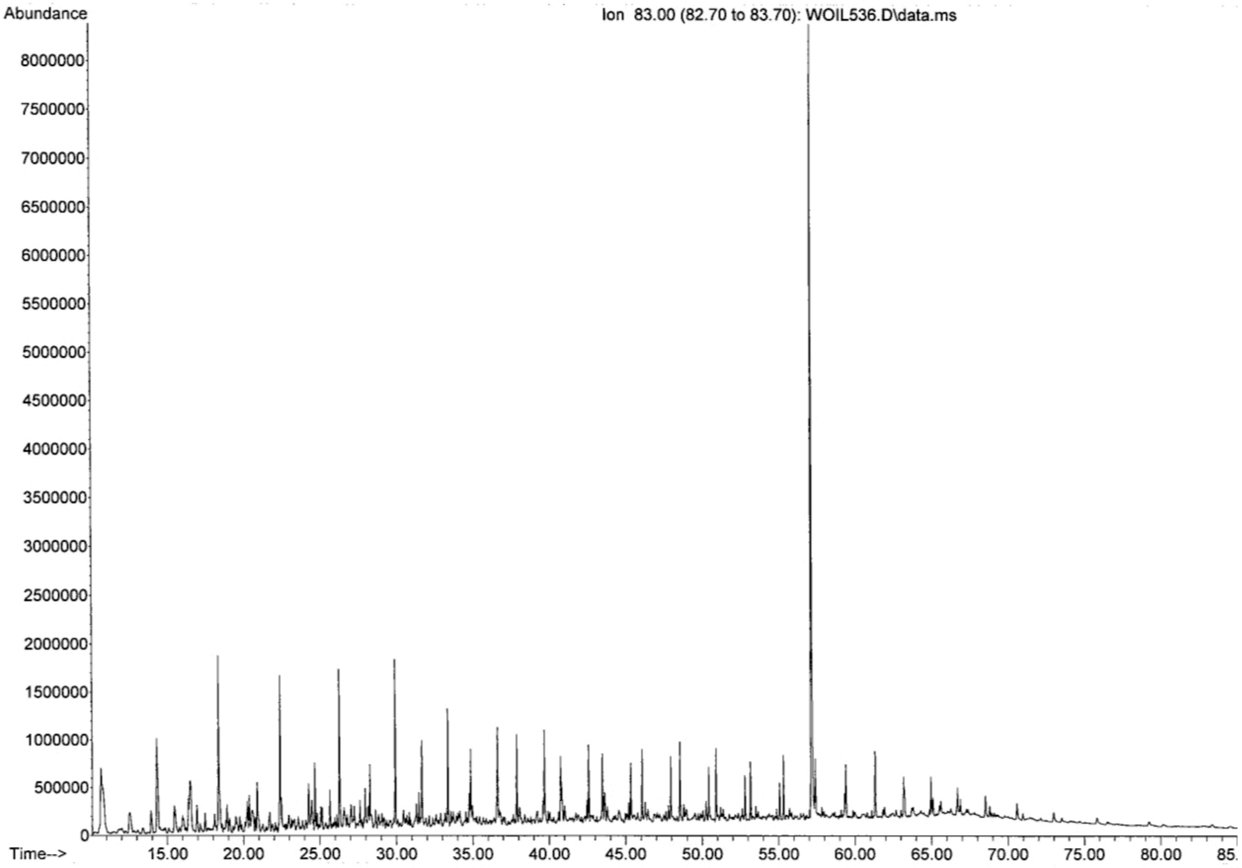
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1000000
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25.00
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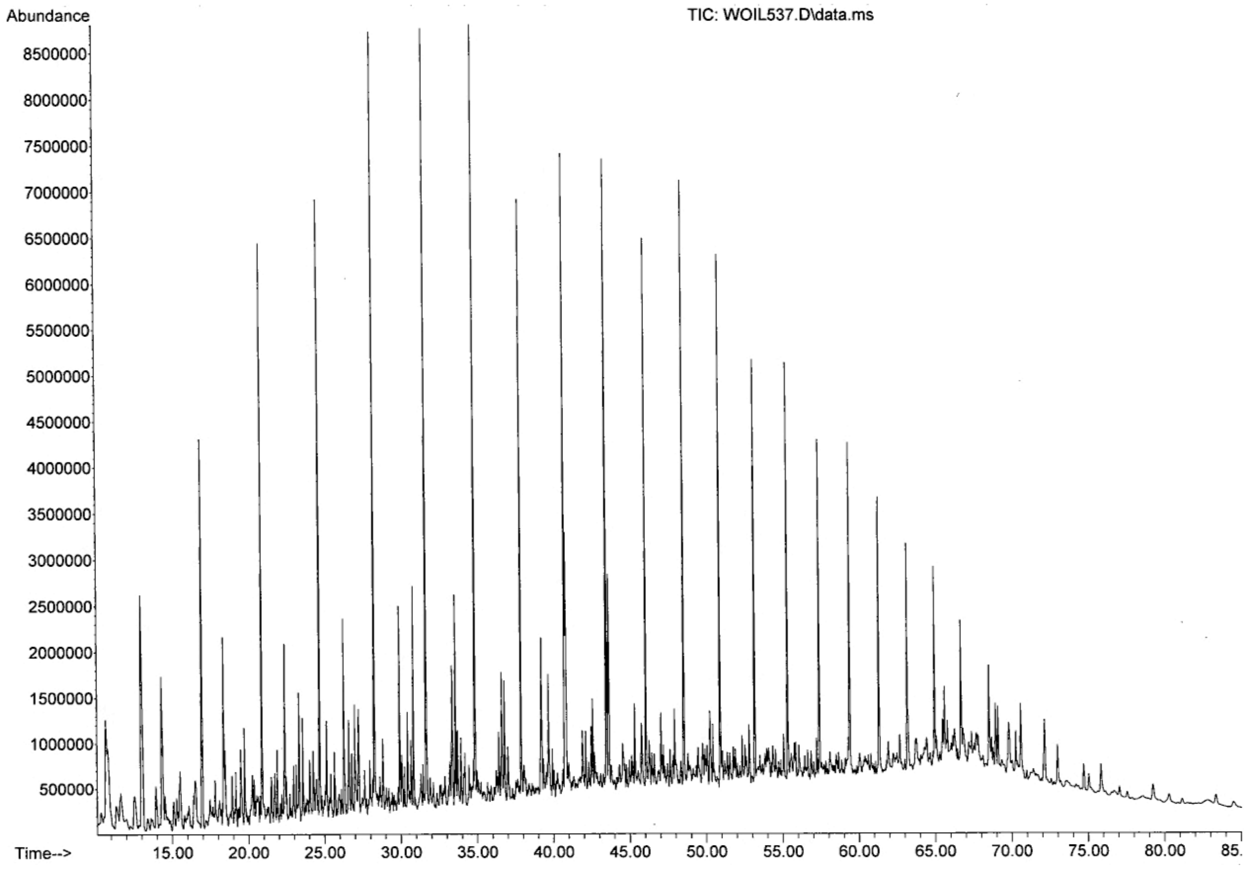
85.

Bruch 1 Gas Chromatograms



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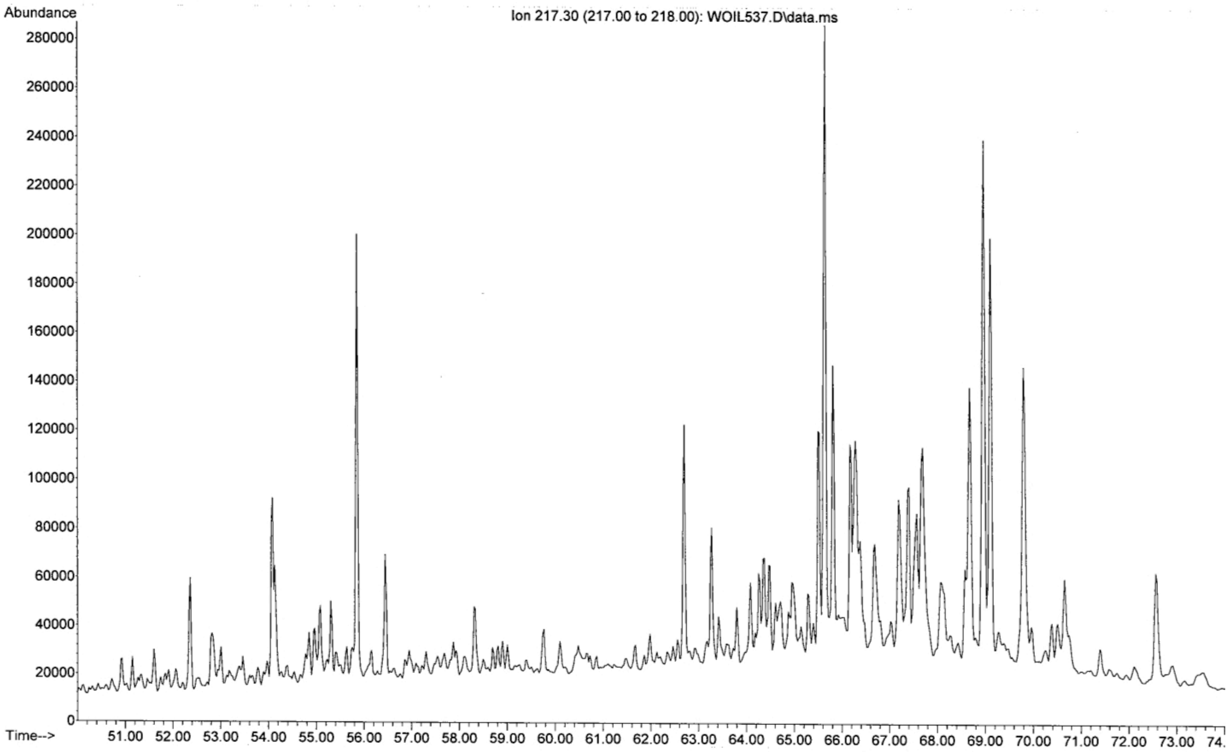

Abundance
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Time-->
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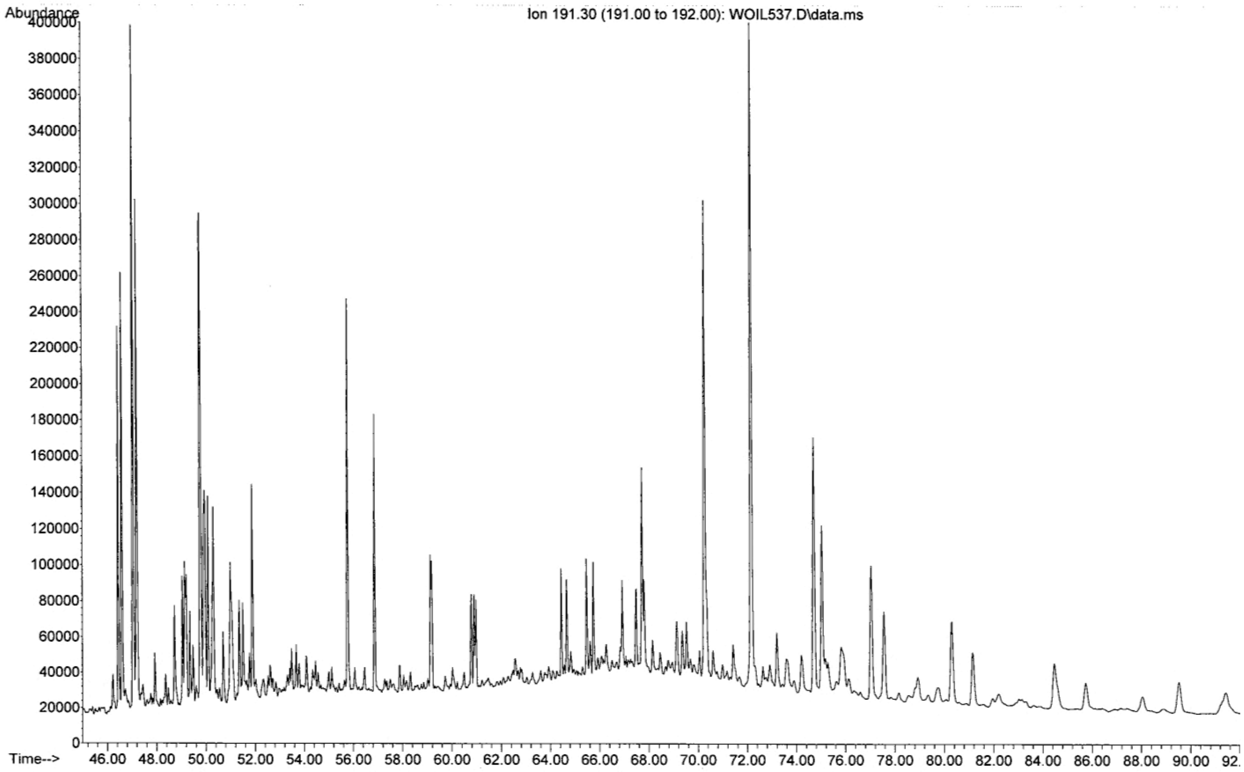
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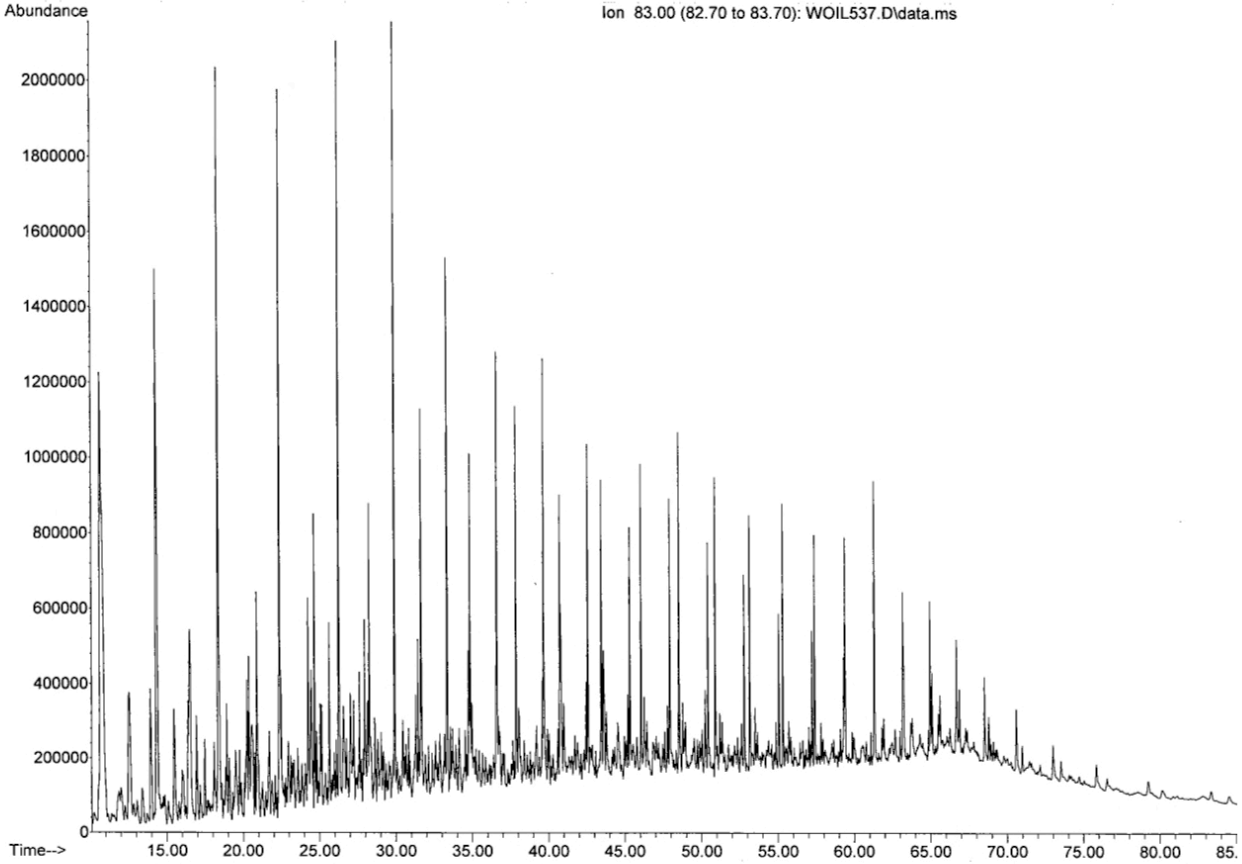
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200000
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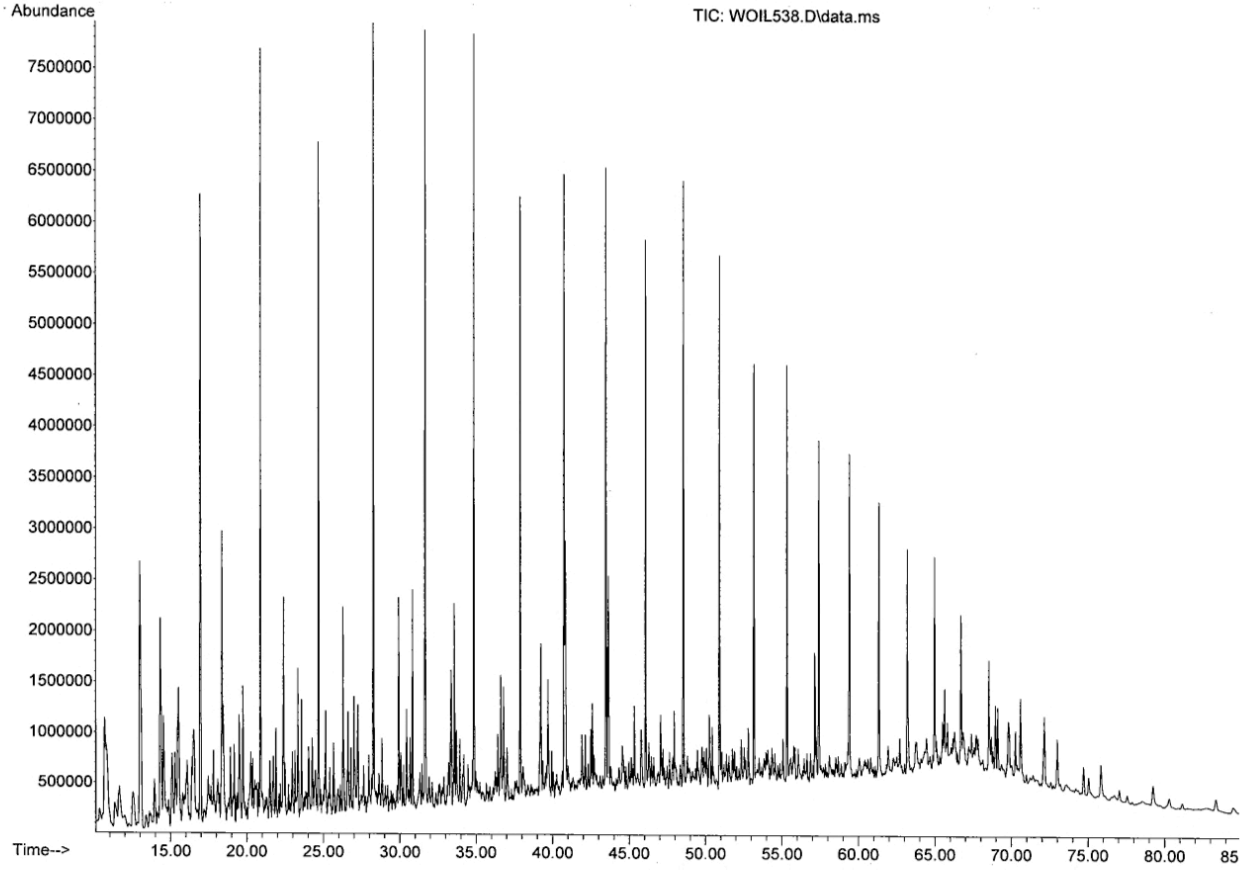
85.

Bruch 2 Gas Chromatograms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2000000
1500000
1000000
500000
Time-->
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20.00
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40.00
45.00
50.00
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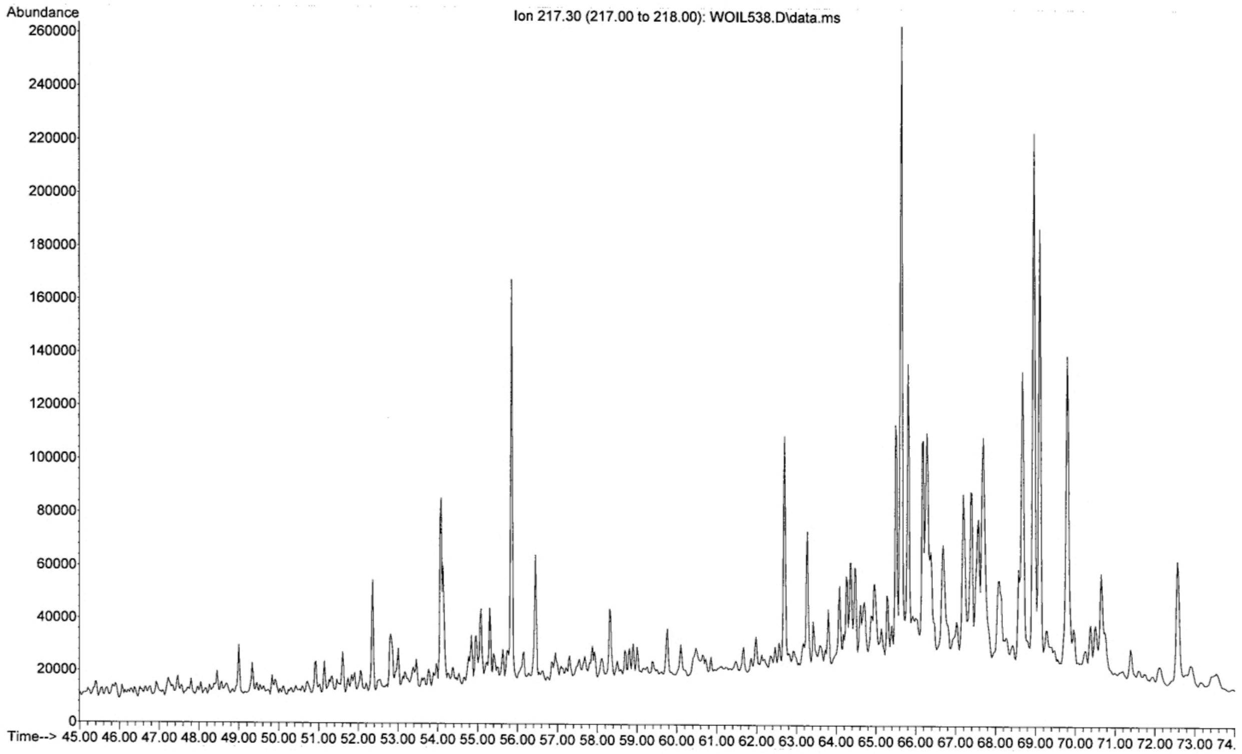
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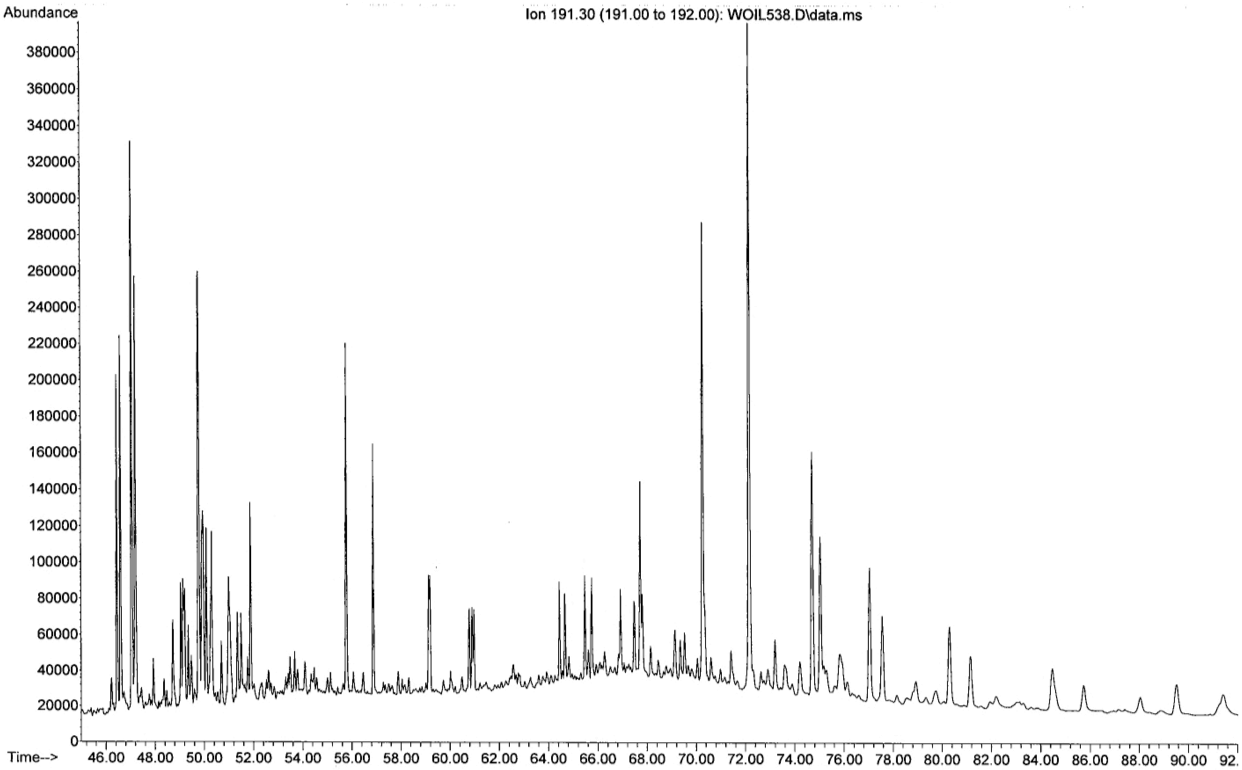
100000
80000
60000
40000
20000
0
Time--> 45.00 46.00 47.00 48.00 49.00 50.00 51.00 52.00 53.00 54.00 55.00 56.00 57.00 58.00 59.00 60.00 61.00 62.00 63.00 64.00 65.00 66.00 67.00 68.00 69.00 70.00 71.00 72.00 73.00 74.


Abundance
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160000
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100000
80000
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40000
20000
0
Time-->
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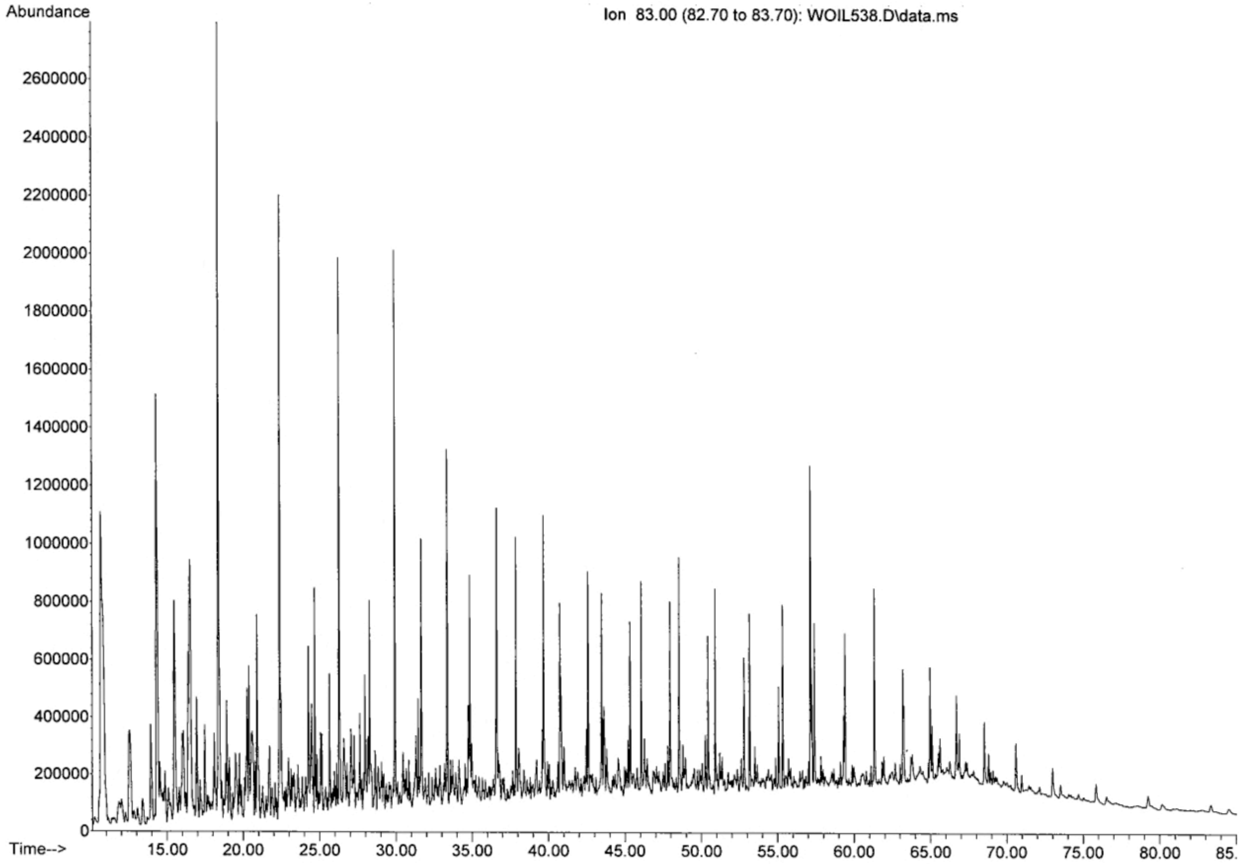
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400000
200000
0
Time-->
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25.00
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55.00
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65.00
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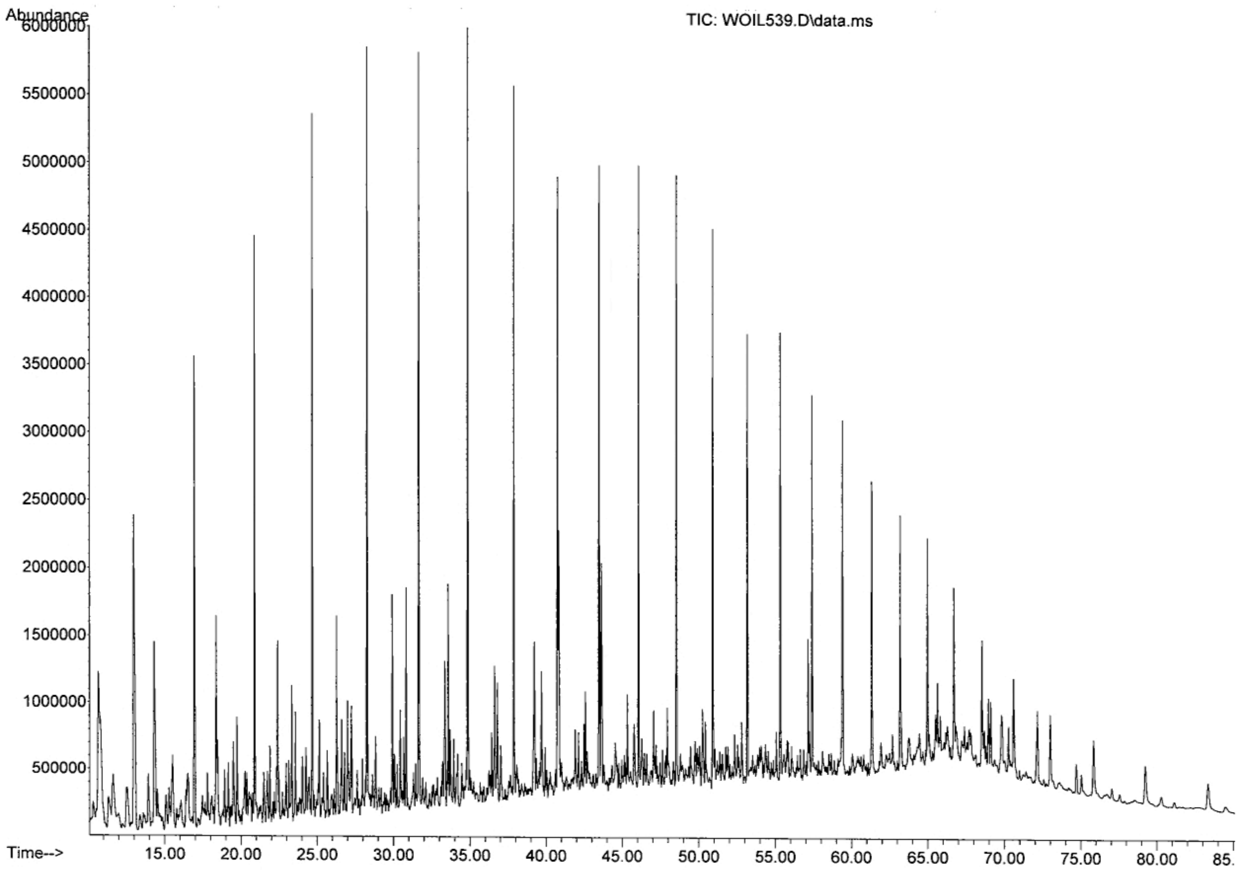
85.

Maple E2 Gas Chromatograms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1000000
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Time-->
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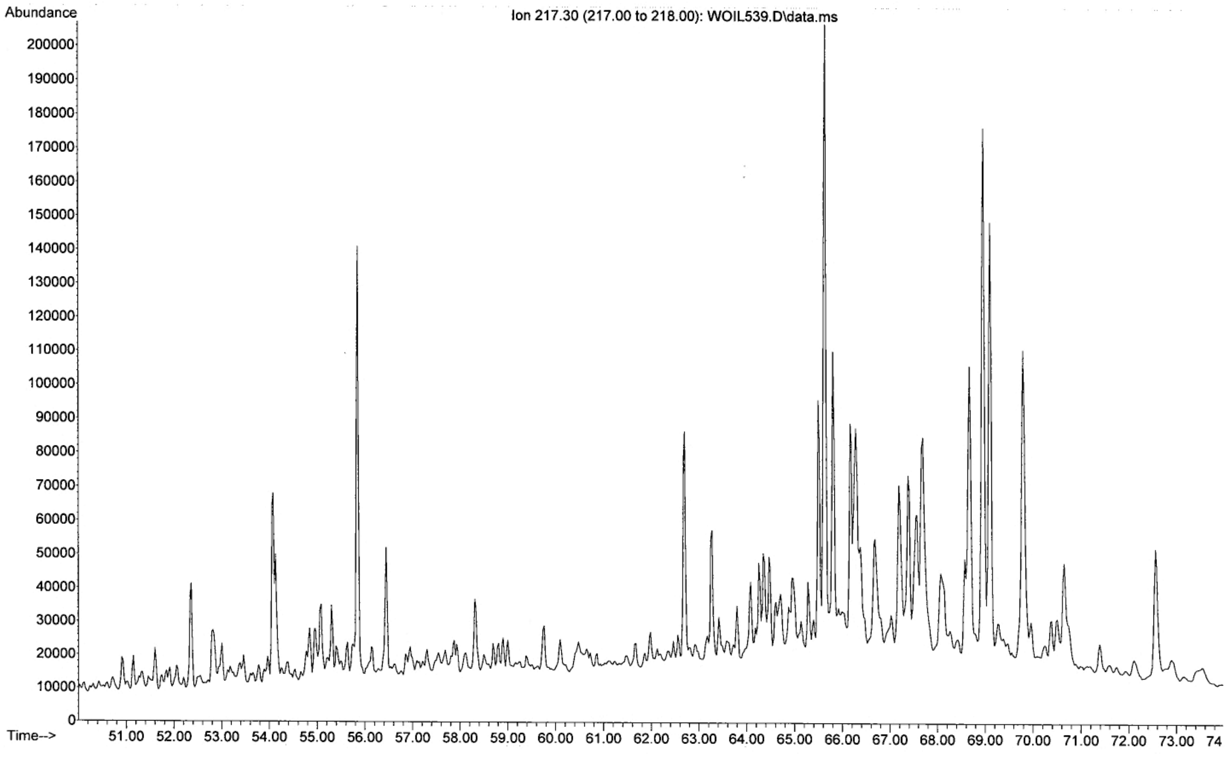
80.00
85.


Abundance
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120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Time-->
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72.00
73.00
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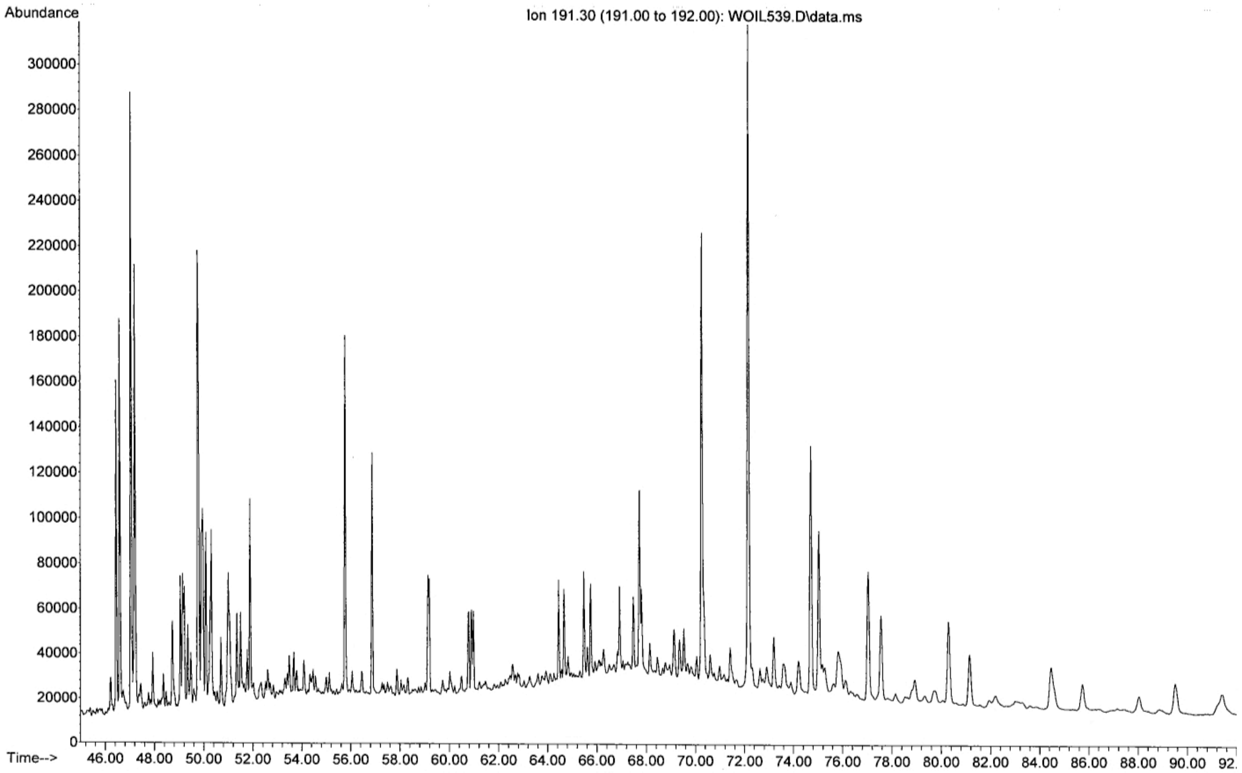
Abundance
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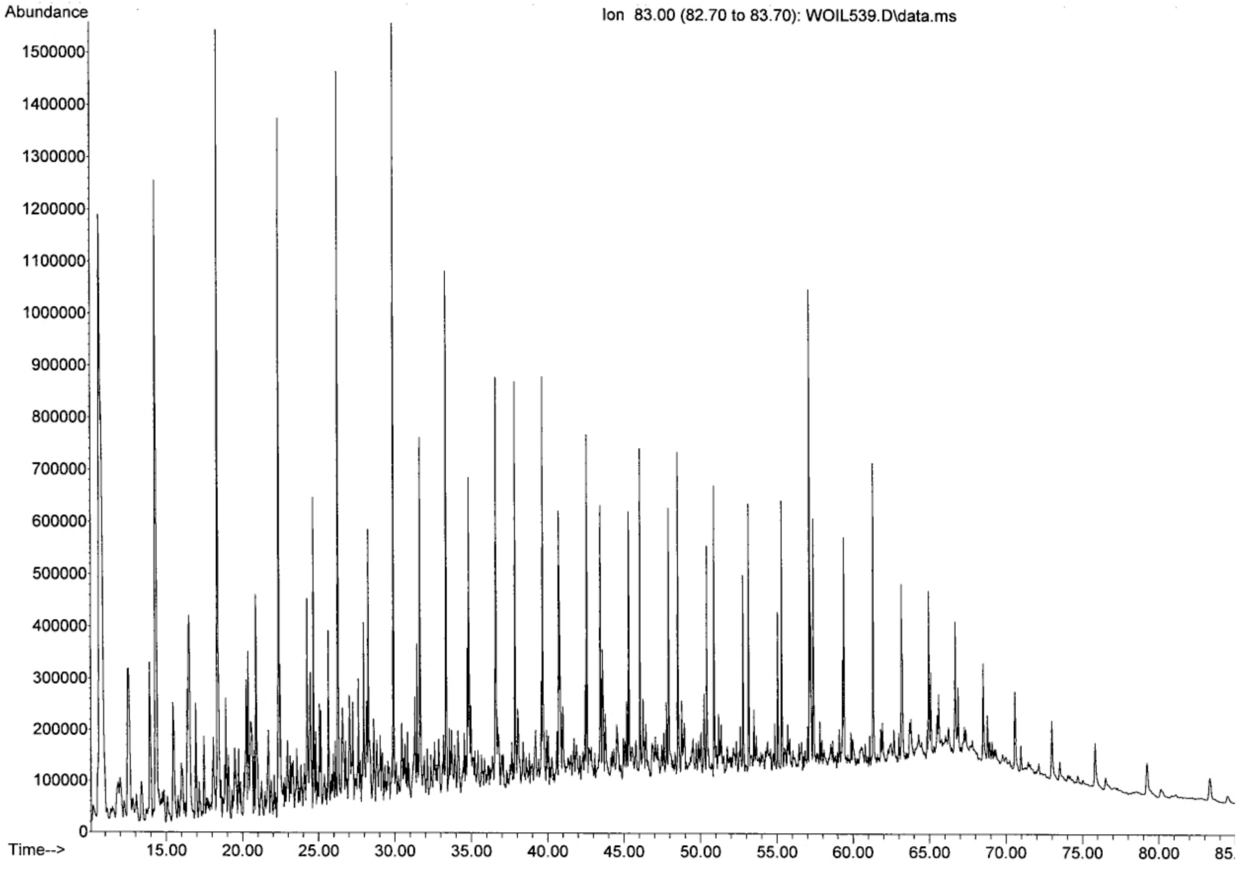
160000
140000
120000
100000
80000
60000
40000
20000
0
Time-->
46.00 47.00 48.00 49.00 50.00 52.00 54.00 56.00 58.00 60.00 62.00 64.00 66.00 68.00 70.00 72.00 74.00 76.00 78.00 80.00 82.00 84.00 86.00 88.00 90.00 92.


Abundance
Ion 83.00 (82.70 to 83.70): WOIL539.D\data.ms
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800000
700000
600000
500000
400000
300000
200000
100000
0
Time-->
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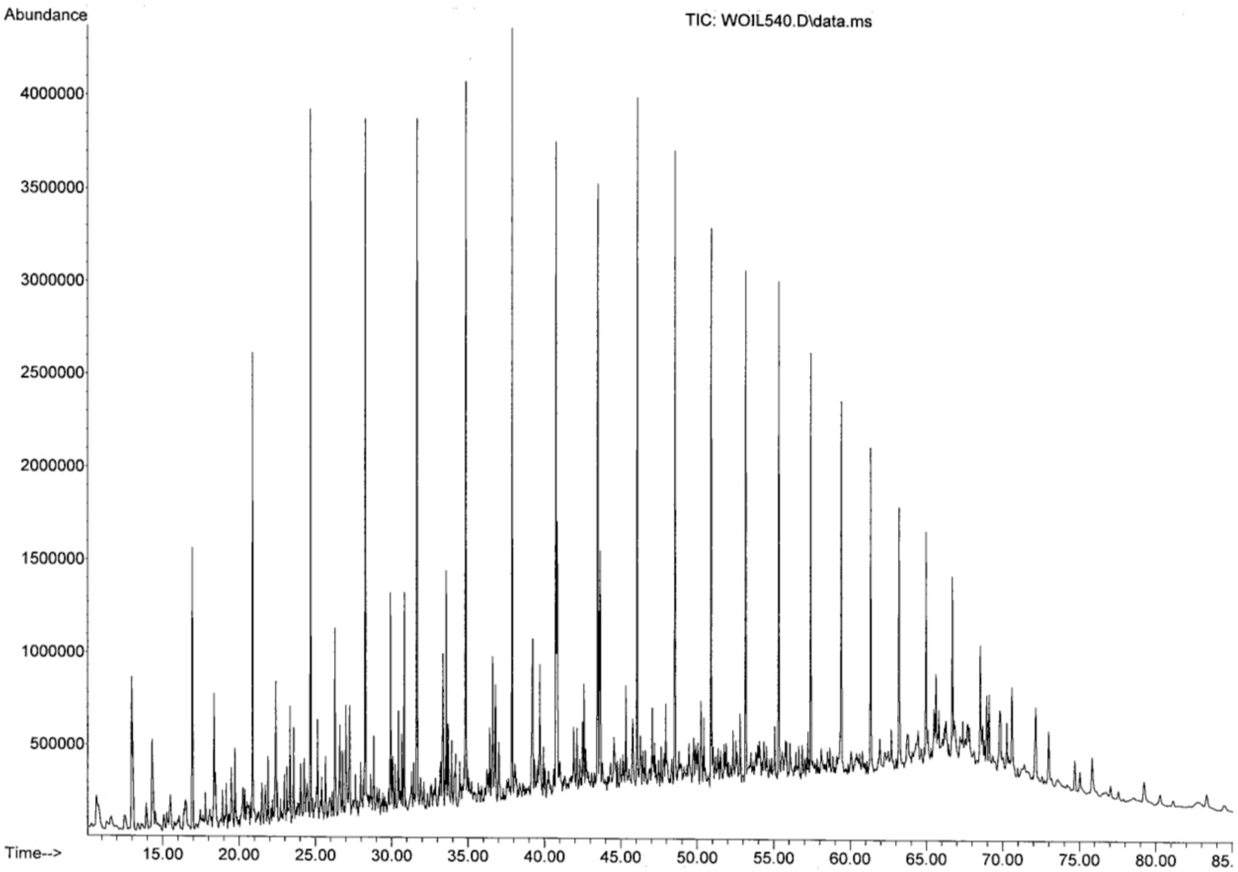
Maple F1 Gas Chromatograms


Abundance
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1000000
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Time-->
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45.00
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55.00
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65.00
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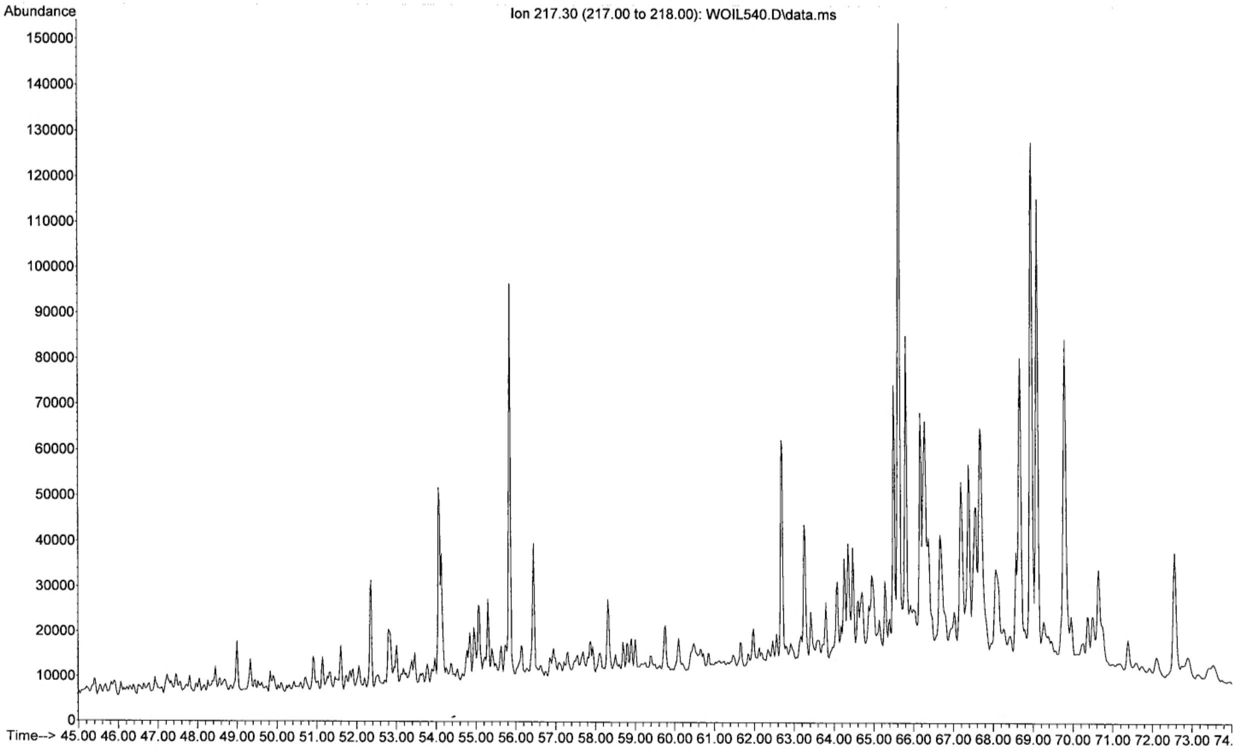
80.00
85.


Abundance
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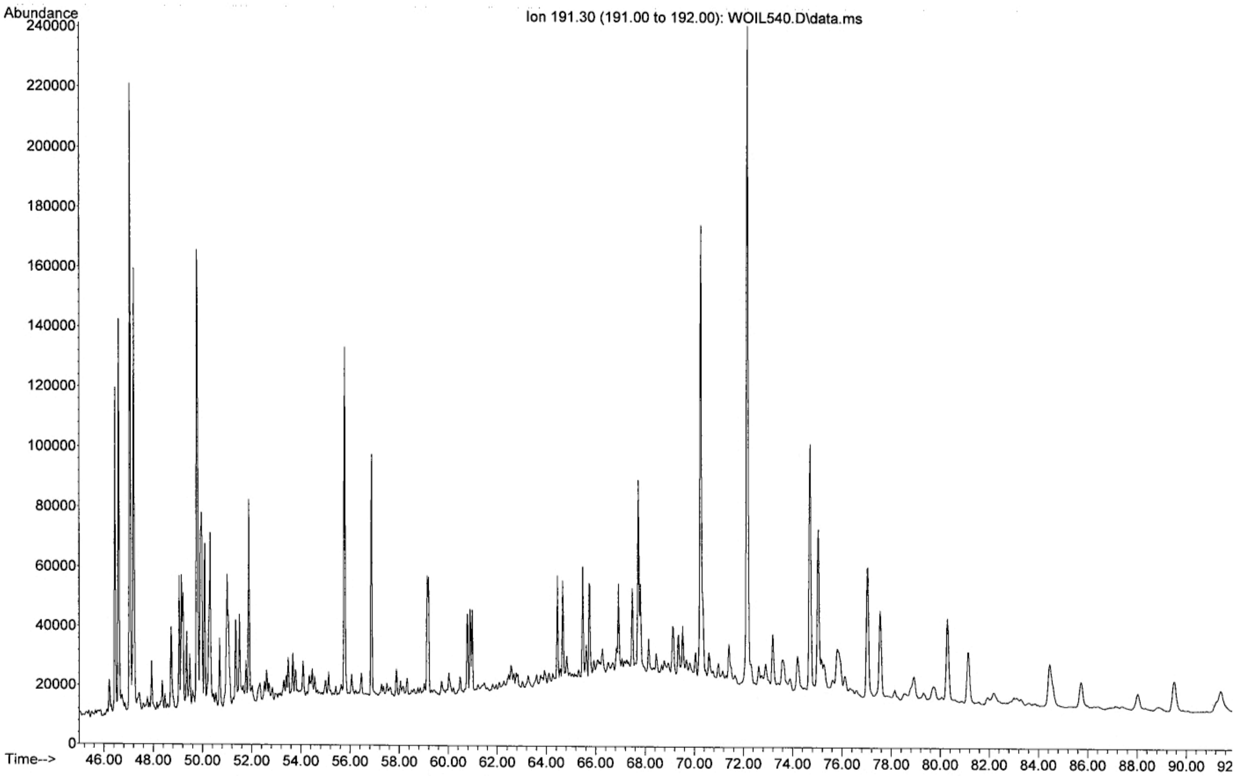
10000
0
Time--> 45.00 46.00 47.00 48.00 49.00 50.00 51.00 52.00 53.00 54.00 55.00 56.00 57.00 58.00 59.00 60.00 61.00 62.00 63.00 64.00 65.00 66.00 67.00 68.00 69.00 70.00 71.00 72.00 73.00 74.



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180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Time-->
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48.00
50.00
52.00
54.00
56.00
58.00
60.00
62.00
64.00
66.00
68.00
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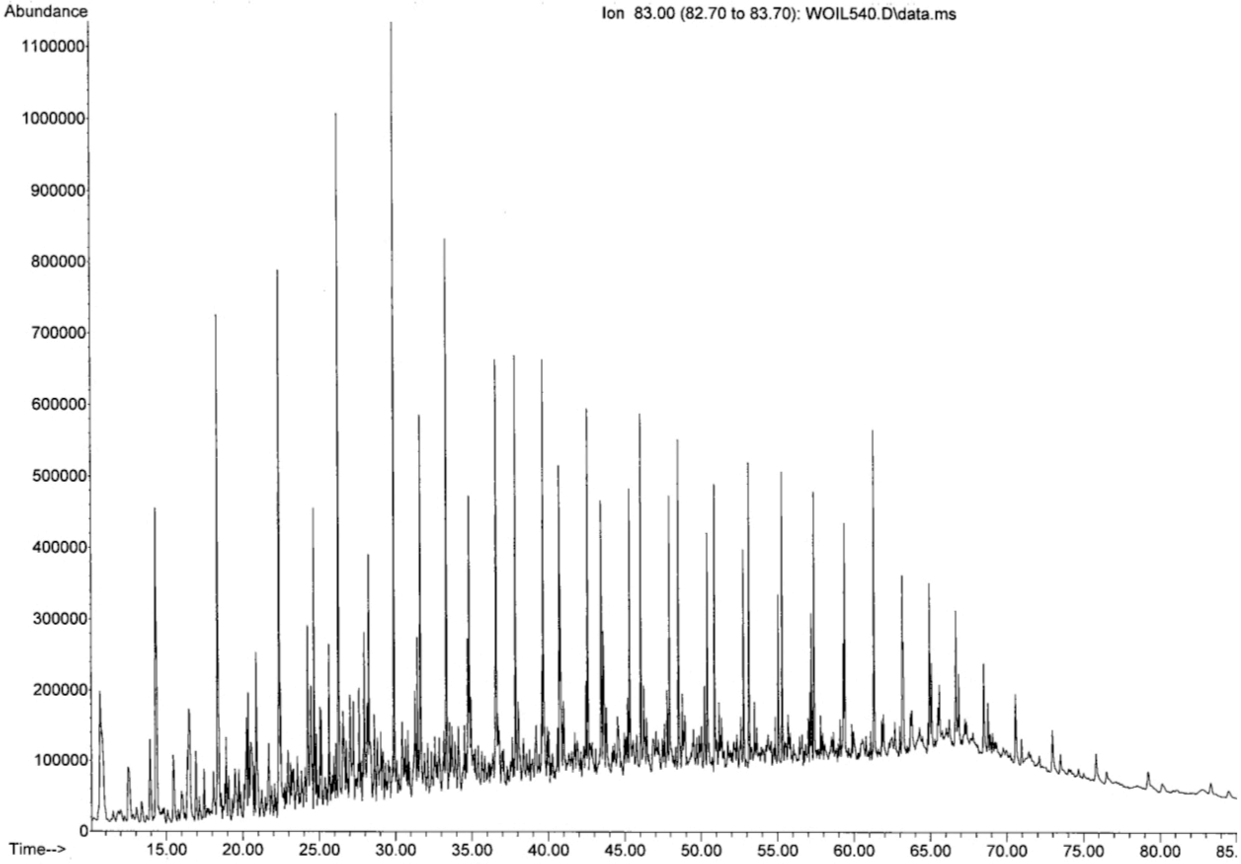
84.00
86.00
88.00
90.00
92



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500000
400000
300000
200000
100000
0
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20.00
25.00
30.00
35.00
40.00
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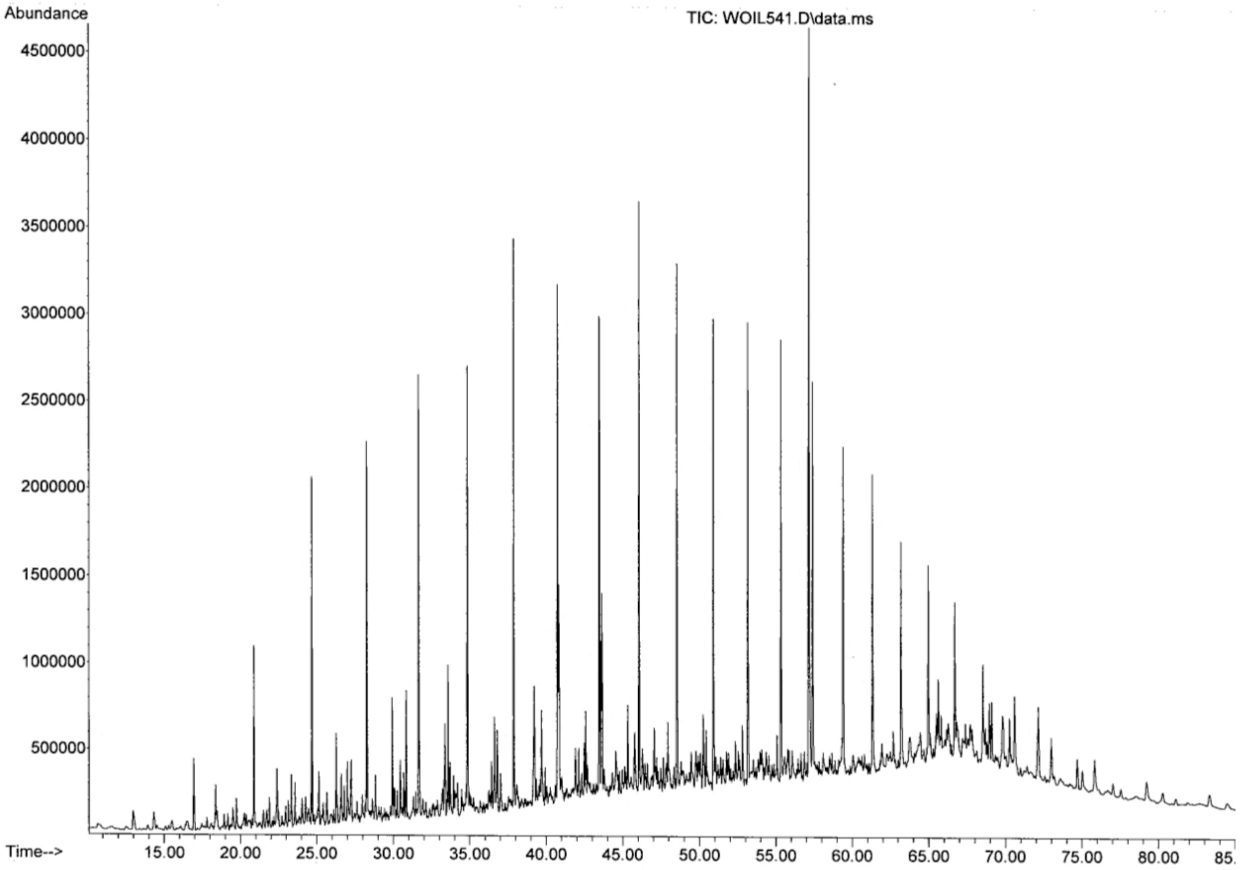
50.00
55.00
60.00
65.00
70.00
75.00
80.00
85.

Maple F2 Gas Chromatograms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TIC: WOIL541.D\data.ms
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Time-->
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25.00
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45.00
50.00
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65.00
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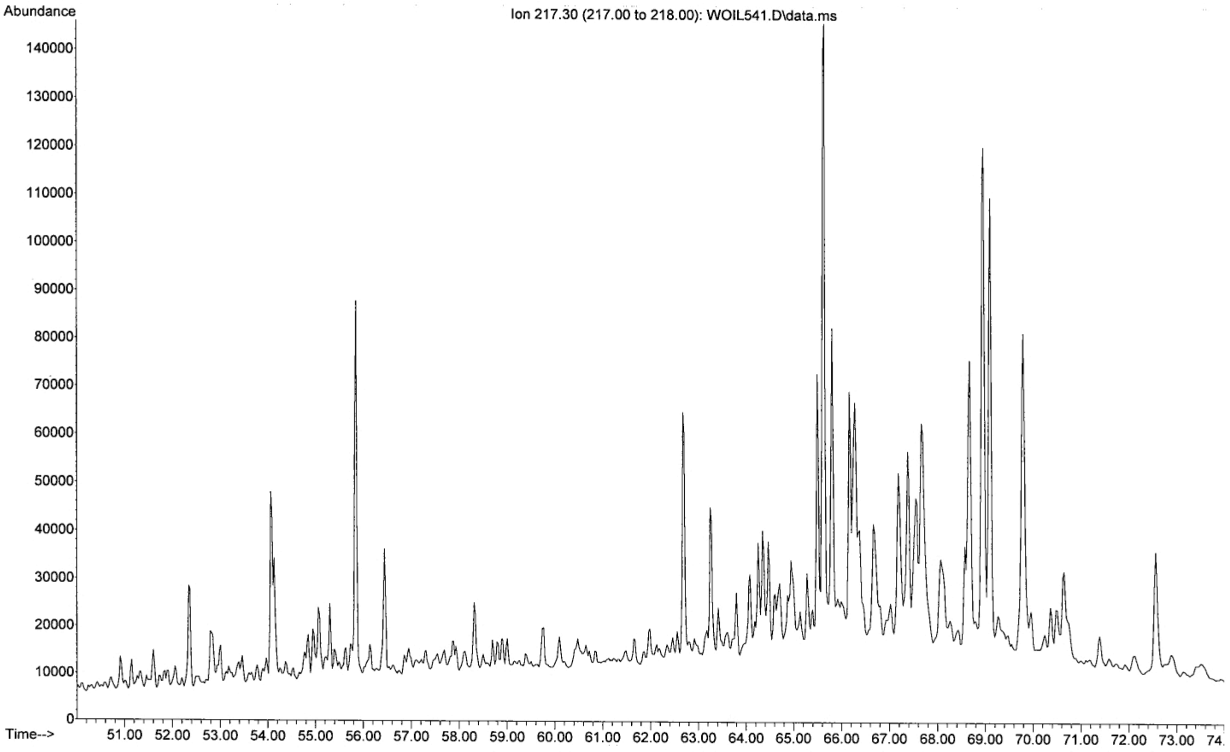
75.00
80.00
85.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70000
60000
50000
40000
30000
20000
10000
0
Time-->
51.00
52.00
53.00
54.00
55.00
56.00
57.00
58.00
59.00
60.00
61.00
62.00
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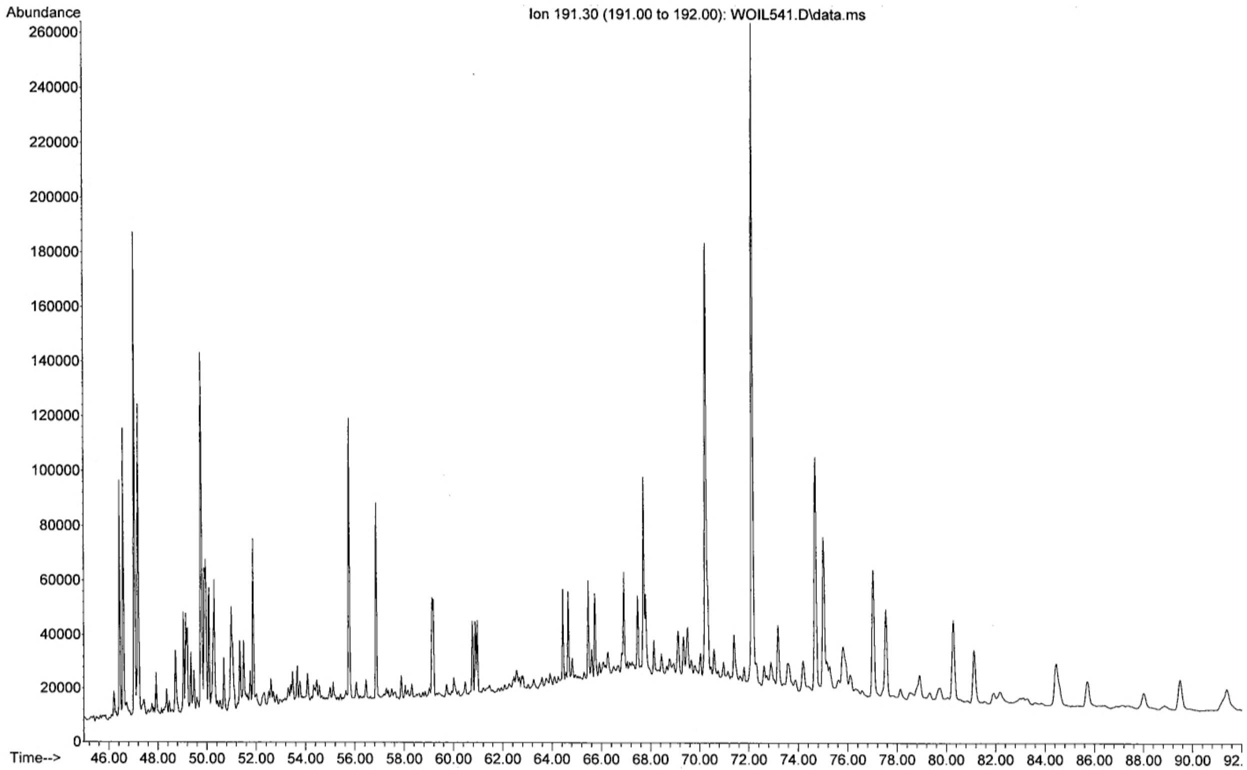
71.00
72.00
73.00
74.


Abundance
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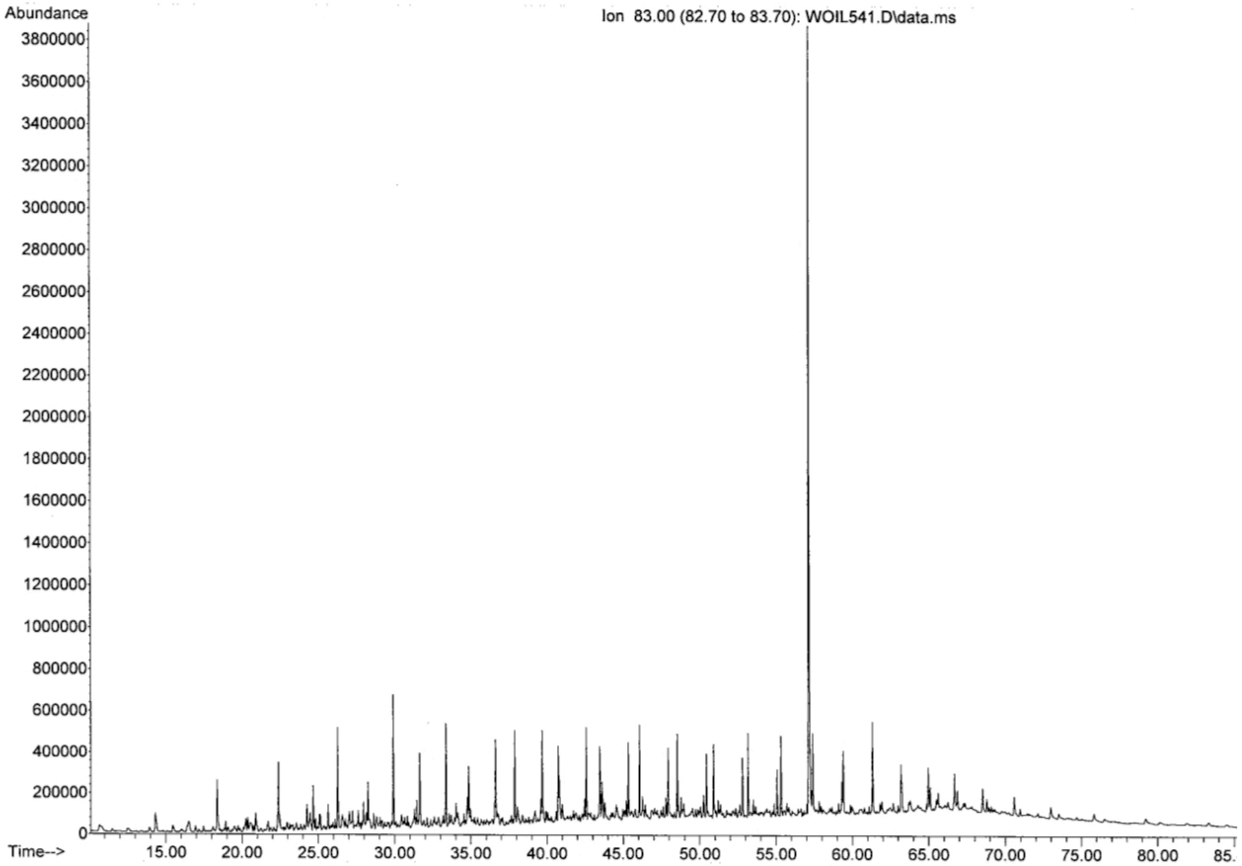
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Time-->
46.00 48.00 50.00 52.00 54.00 56.00 58.00 60.00 62.00 64.00 66.00 68.00 70.00 72.00 74.00 76.00 78.00 80.00 82.00 84.00 86.00 88.00 90.00 92.


Abundance
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2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
Time-->
15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.00 80.00 85.

Table A.5. Geochemical parameters describing crude oil source type (modified from Peters, et al., 2005)

	Marine Carbonate	Marine Shale	Values Found
Pr/(Pr+Ph)	0.5-0.55	0.6-0.66	0.53
Carbon Preference Index	> 1	<1	0.87
Pr/Ph	<1	>1	1.16
Ph/n-C_{18}	<0.3	>0.3	0.38
Pr/n-C_{17}	<0.5	<0.5	0.43
Diasteranes/Steranes	Low	High	0.27
C_{29}/C_{30}	High (>1)	Low	0.72
Sterane Preference	$C_{27}>C_{29}$	$C_{27}<C_{29}$	$C_{27}<C_{29}$
Ts/(Ts+Tm)	Low	High	0.27/Low

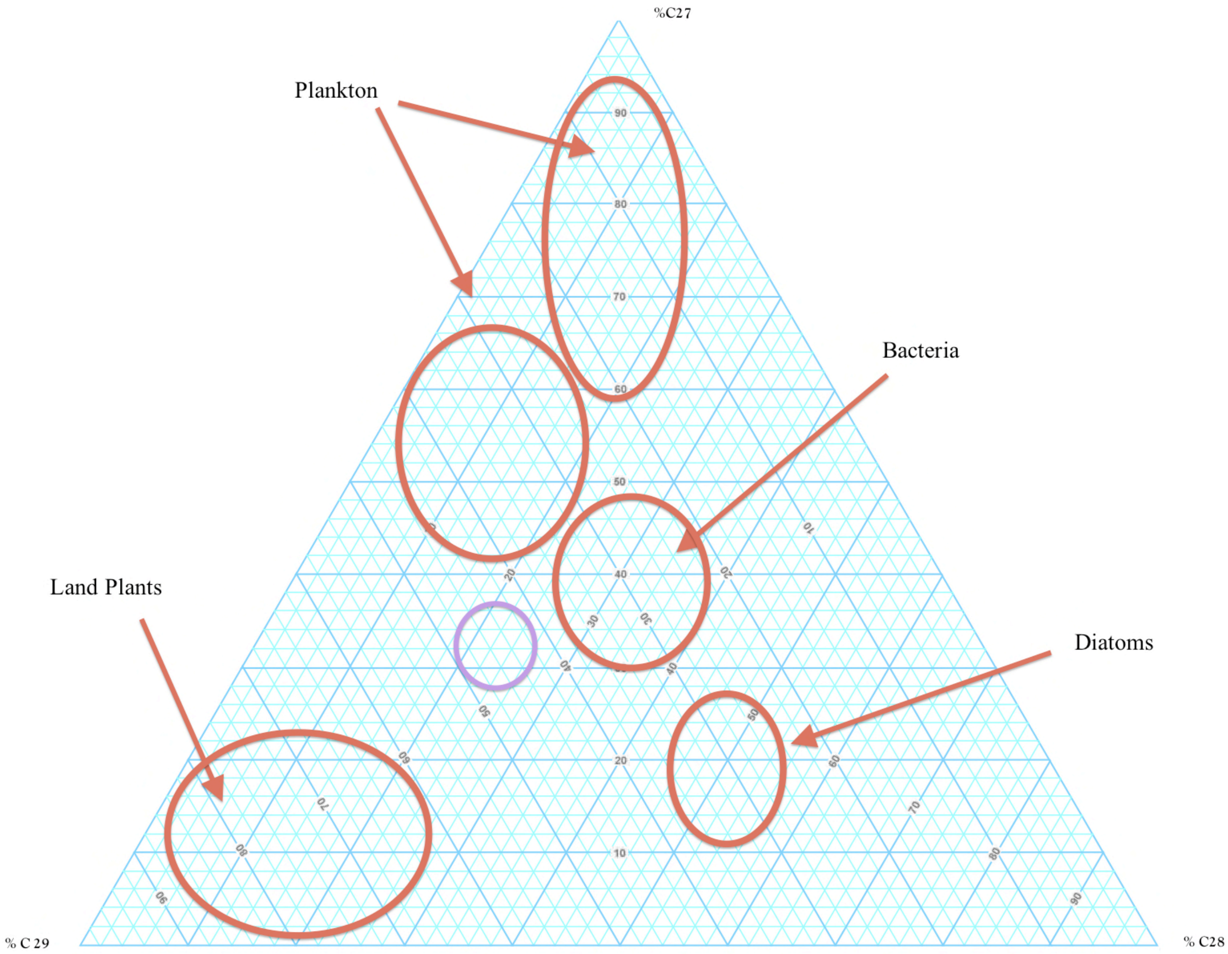

Figure A6. Ternary diagram of the C_{27-29} steranes used in source evaluations. Samples fell within purple circle.