Esso Hatteras Light #1 well
(NCGS # DR-OT-01-46; API 32-055-00001)
Dare County, North Carolina, and
Mobil State of North Carolina #3 well
(NCGS #HY-OT-01-65; API 32-095-00009)
Hyde County, North Carolina:
Geochemical and organic petrology data report

By

Jeffrey C. Reid

North Carolina Geological Survey
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Contents

Appendix 1 – Weatherford contract report - "Geochemical Evaluation of Lower Cretaceous sedimentary rocks in two wells, Atlantic Coastal Plain, North Carolina, USA, prepared November 20, 2012 for the North Carolina Geological Survey." The Weatherford Laboratories primary contributors were: Tim Ruble (petroleum geochemistry), Wayne Knowles (organic petrology), Elizabeth Roberts (compiler), and Gabriel Rotberg (Isologica Data Processing). The Weatherford Laboratories Study Project report is No. BH-94252, 40p.

Appendix 2 - Pyrolysis reports (Total organic carbon [TOC] and Rock-Eval 6 [RE6])

- Hatteras Light #1 well RE6 pyrograms
- Mobil State of North Carolina #3 RE6 pyrograms
- Hatteras Light #1 well TOC data
- Mobil State of North Carolina #3 TOC data
- Hatteras Light #1 well – representative vitrinite trend and reworked vitrinite populations

Appendix 3 - Vitrinite reflectance (photomicrographs, $\%R_o$, whole rock percentages)

- Hatteras Light #1 photomicrographs
- Hatteras Light #1 $\%R_o$ measurements
- Hatteras Light #1 $\%R_o$ whole rock percentages

Acknowledgements

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Abstract

This report releases the original geochemical evaluation report for the 2017 contract study of the Esso Hatteras Light #1 well (NCGS # DR-OT-01-46; API 32-055-00001), Dare County, North Carolina (**Hatteras Light #1** well). Later the Mobil State of North Carolina #3 well (NCGS #HY-OT-01-65; API 32-095-00009); Hyde County, North Carolina (**Mobil #3** well) in Pamlico Sound was added to the current study. The **Hatteras Light #1** was the primary focus of the current study. In a previous study, the Mobil #3 well was studied using fluid inclusion stratigraphy (FIS).

The focus of the geochemical and organic petrology investigation was the examination of the Lower Cretaceous rocks in these two wells. The sampled depth from the Hatteras Light #1 well was 7,800-9,140 ft and the sampled depth of the Mobil #3 well as 5,930-7,300 ft. Sampled intervals in both wells were from the late Aptian/early Albian.

Drill cuttings and core from these wells for this study are archived in the North Carolina Geological Survey repository located in Raleigh, North Carolina. Data from the contract report was incorporated into several reports cited herein.

Objectives

The North Carolina Geological Survey (NCGS) undertook a geochemical study to determine: (1) if hydrocarbons reported in a fluid inclusion stratigraphic study in the Mobil State of North Carolina #3 (Mobil #3) (**Coleman *et al*., 2014**), and oil shows reported in post-drilling examination of cuttings and cores in the Esso Hatteras Light #1 (Hatteras Light #1) well were *in situ* or migrated, and (2) to provide new data on the petroleum potential of the U.S. OCS offshore North Carolina.

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This geochemical evaluation report was commissioned by the North Carolina Geological Survey using state appropriated funds to further the understanding of the hydrocarbon potential in North Carolina. The primary contributors to the Weatherford Laboratories Study Project No. BH-94252 report were: Tim Ruble (petroleum geochemistry), Wayne Knowles (organic petrology), Elizabeth Roberts (compiler), and Gabriel Rotberg (Isologica Data Processing).

The samples for the geochemical and organic petrology data were obtained from existing well cuttings and drill core curated in the North Carolina Geological Survey's repository located in Raleigh, North Carolina. Many of the results of the Weatherford Laboratories study were incorporated into **Reid *et al.* (2018a,b),** and **Post *et al.* (2018).**

Geochemical data and other data obtained

A geochemical investigation of Lower Cretaceous rocks in the Hatteras Light #1 and Mobil #3 wells was conducted using cuttings and conventional core samples from these two wells. The drill core and cuttings were analyzed by a variety of geochemical means, including total organic carbon (TOC, LECO®), programmed pyrolysis (Rock-Eval 6), and organic petrology with measured vitrinite reflectance (%R_o). Selected rock samples with potential hydrocarbon shows were solvent extracted. These extracts were analyzed for gas chromatography (GC) fingerprints and fractional compositions *via* liquid chromatography. Biomarker analyses of the saturate and aromatic fractions were performed using gas chromatography mass spectrometry (GC-MS).

Conclusions

The *in situ* or migrated nature of the hydrocarbons remains problematic. Biomarkers suggest an *in situ* origin. However, in the Hatters Light #1 well, interpreted mobile hydrocarbons were detected at a depth of ~815 ft in Tertiary strata, and solid bitumen and migrabitumen sporadically were identified in Cretaceous rocks. These, the lack of viable source rocks, and low level of thermal maturity suggest their relation to a migration pathway(s), the *"Carolina Ridge Complex*". Both interpretations suggest better hydrocarbon source rock potential and generation–expulsion–migration may have existed farther offshore in deep waters of the Atlantic Outer Continental Shelf (OCS). Sea-surface hydrocarbon seepage slicks identified on satellite synthetic aperture radar images, and hydrocarbon-related diagenetic zones and "chimneys" interpreted on reflection seismic data suggest vertical hydrocarbon migration in this area **Post *et al.*, 2018**; **Reid *et al.*, 2018a,b**.

References

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Post, Paul J.; Reid, Jeffrey C., and Coleman, Jr., James, L., 2018, Petroleum systems of coastal North Carolina: What we know, what we think we know, and the range of uncertainty in the interpretation of geochemical data, *in*, Silva, Ricardo L.; Brown, David E., and Post, Paul J., editors, Conjugate Margins Conference 2018, Program & Abstracts, 19-22 August 2018, Halifax, Nova Scotia, Canada (ISBN 0-9810595-7), p. 119.

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2018, Halifax, Nova Scotia, Canada (ISBN 0-9810595-7), pp. 136-137.

Reid, Jeffrey C.; Coleman, James L., Jr., and Post, Paul J., 2018b, Organic petrology, geochemistry, and stratigraphic data from the Esso Hatteras Light No. 1 and the Mobil State of North Carolina #3 and their effect hydrocarbon prospectivity in coastal North Carolina: North Carolina Geological Survey, Open-File Report 2018-06, 3 panels.

Appendices

Appendix 1 – Weatherford contract report (click here for report)

"Geochemical Evaluation of Lower Cretaceous sedimentary rocks in two wells, Atlantic Coastal Plain, North Carolina, USA, prepared November 20, 2012 for the North Carolina Geological Survey. The Weatherford Laboratories primary contributors were: Tim Ruble (petroleum geochemistry), Wayne Knowles (organic petrology), Elizabeth Roberts (compiler), and Gabriel Rotberg (Isologica Data Processing). The Weatherford Laboratories Study Project report is No. BH-94252, 40p.

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Mobil State of North Carolina #3 TOC data

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Hatteras Light #1 photomicrographs

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Hatteras Light #1 %R_o whole rock percentages

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LABORATORIES

GEOCHEMICAL EVALUATION OF LOWER CRETACEOUS SEDIMENTARY ROCKS IN TWO WELLS, ATLANTIC COASTAL PLAIN, NORTH CAROLINA, USA

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

- The Lower Cretaceous interval evaluated in the Esso #1 and Mobil #3 wells contains poor to fair source material containing dominantly gas-prone Type III organic matter. This source rock interval is interpreted to be immature with regard to the oil generation window. In-situ hydrocarbon saturations (bitumen) are generally low.

- The occurrence of solid hydrocarbons (bitumen/migrabitumen) in the Lower Cretaceous interval has been confirmed and documented via organic petrology. This material exhibits weak brown fluorescence and the occurrence of all organic material (kerogen macerals and bitumen) in these rocks is quite dispersed. Thermal maturity assessed on the basis of both measured vitrinite reflectance and equivalent solid bitumen reflectance in the Lower Cretaceous is ~0.5% VRo.

- Biomarker analyses of composite cuttings samples from the Lower Cretaceous interval in these two wells show that the extractable hydrocarbons contain input from both terrigenous and marine organic matter deposited in a fairly oxic depositional environment. The biomarkers appear to originate from marine shale source rocks and are low thermal maturity, with the Esso #1 well having immature biomarker ratios and the Mobil #3 well having ratios in the immature/early mature range.

- The presence of the age-specific biomarker oleanane in both of these samples suggests that the extractable hydrocarbons are likely to be Cretaceous age, although an origin from migrated Jurassic aged oil cannot be entirely ruled out.

- The irrefutable source of the hydrocarbons present in the Lower Cretaceous intervals within the Esso #1 and Mobil #3 wells is inconclusive due to conflicting suggestions from different data sources. However, based on the extremely low concentrations and sporadic nature of hydrocarbons in the samples which have been examined, there is no evidence for either substantial in-situ generation or a significant migration pathway.

GEOCHEMISTRY

A geochemical investigation has been conducted to examine the Lower Cretaceous rocks in two wells from the Atlantic Coastal Plain, North Carolina, USA (Table 1). Cuttings and conventional core samples from these wells were analyzed by a variety of geochemical techniques, including total organic carbon (TOC, LECO®), programmed pyrolysis (Rock-Eval 6), and organic petrology with measured vitrinite reflectance (Ro). Select rock samples with potential hydrocarbon shows were solvent extracted. These extracts were analyzed for gas chromatography (GC) fingerprints and fractional compositions via liquid chromatography. Biomarker analyses of the saturate and aromatic fractions were performed using gas chromatography mass spectrometry (GC-MS). The complete results of these analyses are documented in this report along with a summary geochemical interpretation that also incorporates select published geochemical data (Coleman et al., 2014; Coffey and Sunde, 2009) and unpublished organic petrology data (M. Malinconico, per. comm., 2017).

API Number	Well Name	Sampled Depth (ft.)	Stratigraphic Intervals
32-055-00001	Hatteras Light (Esso #1)	7800 – 9140	late Aptian/early Albian
32-095-00009	State of N.C. #3(Mobil #3)	5930 – 7300	late Aptian/early Albian

Table 1. Well Information

GEOCHEMICAL SCREENING

Routine total organic carbon (TOC) was measured using the LECO TOC analyzer and programmed pyrolysis was performed with the Rock-Eval 6. In addition, organic petrology data for samples from the entire penetrated interval of the Esso #1 well has been incorporated into the interpretation presented in this report. In the Mobil #3 well, organic petrology was only conducted on select samples from the Lower Cretaceous interval due to budgetary constraints.

The TOC and programmed pyrolysis data are useful for screening for potential petroleum source rocks (Table 2). The data define the quantity, quality, and thermal maturity of organic matter present in the rocks (Peters, 1986). We employ the following guidelines from Peters et al. (2005) for the interpretations of geochemical screening data presented in this report:

Generative Potential	TOC (weight %)	S1 (mg HC/g rock)	S2 (mg HC/g rock)
Poor	<0.5	<0.5	<2.5
Fair	0.5 – 1.0	0.5 – 1.0	2.5 – 5.0
Good	1.0 – 2.0	1.0 – 2.0	5.0 – 10.0
Very Good	2.0 – 4.0	2.0 – 4.0	10.0 – 20.0
Excellent	>4.0	>4.0	>20.0

Table 2. Generative Potential (Quantity of organic matter)

Bear in mind that these guidelines are qualitative and empirical. The average TOC of petroleum source rocks worldwide is 1.8 wt.%, of shale source rocks 2.2 wt.%, and of carbonate source rocks 1.9 wt.% (Jones, 1984; Miles, 1989). Petroleum source rocks also need a minimum TOC of about 1.5 – 2.0 wt.% before expulsion can occur during thermal maturation (Pepper, 1991; Lewan, 1994). For these reasons, many petroleum geochemists regard 2.0 wt.% as a minimum TOC value for defining *economic* source rocks and viable resource play reservoirs, although 1.0 wt.% TOC continues to be used as the minimum cut off for an *effective* source rock (meaning a unit that can both generate and expel hydrocarbons, but which may not be of significant volume to be commercial).

The normalized oil content, NOC, is calculated by normalizing the ratio of S1/TOC. This value is also called the Oil Saturation Index (OSI) by Jarvie (2012). Interpretive guidelines for NOC are:

- 0 – 50: oil-lean
- 50 – 100: possible oil staining or show; mature, tight petroleum source rock
- >100: reservoirs or contamination.

These guidelines are for conventional reservoirs; in unconventional reservoirs, Jarvie (2012) considers a NOC value > 100 mg hydrocarbon/g TOC as potentially productive.

Kerogen types are generally grouped into five basic categories (Table 3). Type I and II kerogens generate dominantly oil with minor amounts of primary associated gas. Type II/III is a mixed kerogen type that has the potential to generate both oil and gas. Type III kerogens mainly generate gas, with only a small amount of typically waxy oil, while Type IV kerogens have little or no remaining potential to generate hydrocarbons.

Kerogen type	Hydrogen Index (HI) mg HC/g TOC	S2/S3	Main product at peak maturation
I	>600	>15	Oil
II (II-S)	300 – 600	10 – 15	Oil
II/III	200 – 300	5 – 10	Mixed oil and gas
III	50 – 200	1 – 5	Gas
IV	<50	<1	None

Table 3. Kerogen Type and Expelled Product (Quality of organic matter)

The type of kerogen present is dependent on the type of primary organic matter and is also an indication of the source rock depositional environment. Well preserved algae typically dominate in Type I kerogen, which usually indicate a lacustrine depositional environment (but are also sometimes found in specific marine settings). Type II kerogen is deposited exclusively in marine conditions and contains dominant amorphous organic matter (AOM) along with cutinites, plant spores, exinites and resins. During initial maturation, Type I & II source rocks generate mainly oil and only a limited amount of gas. As maturation proceeds through higher temperatures, secondary cracking in these source rocks alters the generated oil into gas. Type III organic material is comprised of vitrinite and is typically woody material found in continental rocks deposited in swamps, rivers and deltas, but it can also be found in marine environments where it is washed in from a nearby shelf and often results in mixed Type II/III kerogen. Type IV kerogen contains inertinite, where oxidation of organic material has occurred, either before deposition or in-situ.

Caution should be exercised when using the pyrolysis kerogen quality parameters. The kerogen type designations are mainly based on optical characteristics defined by organic petrology. The HI and S2/S3 values are laboratory chemical quantities calculated from the TOC and pyrolysis results. A common problem with interpreting kerogen type from the pyrolysis data is that the laboratory results reflect hydrogen content of the organic matter and not necessarily the maceral type. For example, both oxidation and reworking of kerogen, and increasing thermal stress, lower the HI value even if the organic material was deposited as hydrogen-rich Type I or Type II kerogen. Also, in this study very lean TOC content can adversely impact calculated parameters like HI and reported values should be interpreted cautiously.

Thermal maturity guidelines based upon organic petrology (measured vitrinite reflectance %VRo) and programmed pyrolysis are shown in Table 4. The T_{max} values listed above are general with regard to maturity. The maturity scale is kerogen-type-dependent (see Huc, 2013, p. 109 – 110). For example, some Type I kerogen enters the oil window ~ 440° to 442°C and exits at ~ 446° to 448°C due to the very narrow range of activation energies for this type of organic matter. Terrigenous organic matter dominated by Type III kerogen has a wider range, entering the oil window ~ 430°C to 435°C and exits at ~ 466° to 472°C. Sulfur-rich Type II-S kerogen enters the oil window at ~420°C and exits ~450°C due to the differences in relative bond strength, with S-C bonds being significantly weaker than C-C bonds.

Maturity	%R_o	T_{max} (°C) Type II Kerogen	T_{max} (°C) Type I Kerogen	Production Index
Immature	< 0.50	<425	<440	<0.10
Early Oil	0.50 – 0.65	425 – 435	440 – 442	0.10 – 0.15
Peak Oil	0.65 – 0.90	435 – 445	442 – 446	0.15 – 0.25
Late Oil	0.90 – 1.1	445 – 450	446 – 450	0.25 – 0.35
Condensate/Wet Gas	1.1 – 1.4	450 - 470	450 - 470	>0.40
Dry Gas	>1.4	>470	>470	-

Table 4. Thermal Maturation for Type I and Type II Kerogen.

GENERATIVE POTENTIAL

The Lower Cretaceous samples in both of the wells examined in this study have few zones of elevated organic richness and appear to have poor to fair generative potential (Figure 2 & Figure 3). In the Esso #1 well, the measured TOC values vary from 0.01 wt. % (poor) to as high as 1.05 wt. % (good), with an average value of only 0.17 wt. % (poor). The histogram plot of TOC distributions (Figure 1) illustrate that the dominant population is within the 0.0 to 0.1 wt. % range. Outside of this range there appears to be a general trend of progressive decrease in frequency of samples with increasing TOC content. Only one sample has TOC content above the minimum requirement of 1 wt.% for effective petroleum source rocks. None of these samples have TOC content above the minimum requirement of 2 wt.% for economic petroleum source rocks.

In the Mobil #3 well, the measured TOC values vary from 0.01 wt. % (poor) to as high as 9.30 wt. % (excellent), with an average value of 0.73 wt. % (fair). Bear in mind, that this average TOC value is significantly influenced by the single high TOC in the cuttings sample at 6750-60' depth (Figure 3). It is speculated based upon log characteristics and general sample descriptions that the elevated TOC content in this single sample is likely due to the occurrence of coal or lignite (J. Reid, per. comm.). The histogram plot of TOC distributions (Figure 1) illustrate that the dominant population is within the 0.1 to 0.2 wt. % range. In this well there appears to be a dual population trend with TOC maxima at 0.2 and 0.8 wt. % (Figure 1). This is likely a consequence of a smaller statistical sample set and the fact that this well was not continuously sampled throughout the entire Lower Cretaceous interval (Figure 3). Only five (5) samples have TOC content above the minimum requirement of 1 wt.% for effective petroleum source rocks. As noted previously, there is also one sample that has TOC content above the minimum requirement of 2 wt.% for economic petroleum source rocks. All of these elevated TOC samples occur within the relatively narrow depth range of ~6700-6800', suggesting that this stratigraphic interval may have slightly higher prospectivity for in-situ hydrocarbon generation and expulsion.

Pyrolysis S2 yields in the Lower Cretaceous samples from the two wells examined in this study range from 0.03−5.68 mg HC/g rock or 1−124 bbl/a-ft and are lowest in samples where TOC values are lean (Figure 2 & Figure 3). In the Esso #1 well the S2 yields average only 0.41 mg HC/g rock or 9 bbl/a-ft, while the Mobil #3 well averages slightly higher at 0.65 mg HC/g rock or 14 bbl/a-ft. These values indicate a very low amount of remaining primary hydrocarbon generation potential and are consistent with generally poor preservation of organic matter in these rocks. These samples mostly plot in the region associated with Type III gas-prone terrigenous kerogen (Figure 4), which is fairly consistent with the interpreted original kerogen type based upon select organic petrology. Even the single high TOC sample from the Mobil #3 well which has a relatively high S2 yield plots in the region associated with present day Type III kerogen quality (Figure 4). It should be noted that organic petrology examination of the high TOC sample (6750') did not reveal significant kerogen content, with vitrinite, liptinite and inertinite content all <1% (whole rock basis) suggesting that the TOC value of 9.30% may be anomalous. The organic

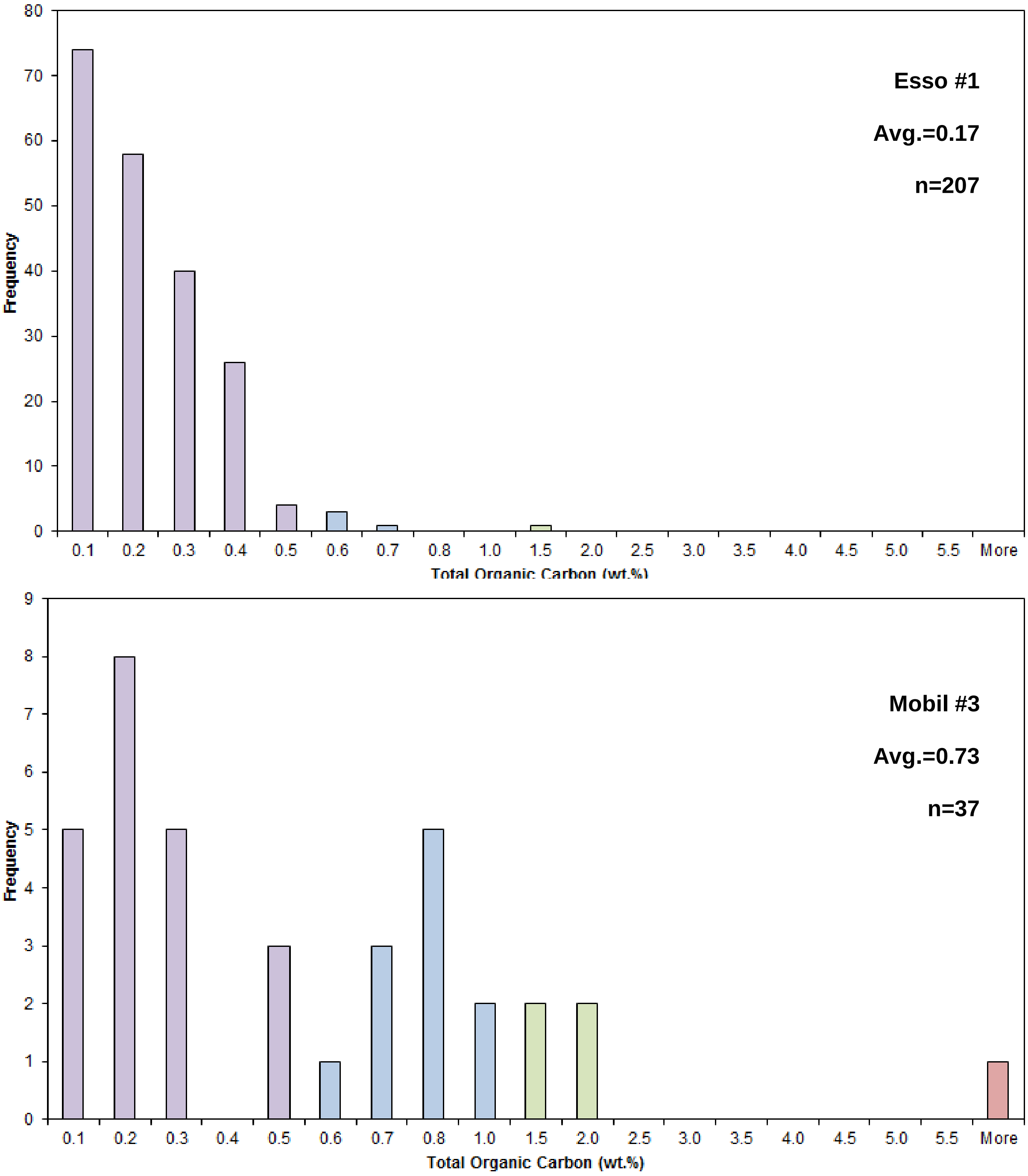

Figure 1.Histogram plot of Total Organic Carbon (TOC) distributions for Lower Cretaceous rocks in the Esso #1 and Mobil #3 wells. Data is organized into 0.1 wt.% TOC bins up to 1 wt.% and 0.5 wt.% TOC bins beyond, thus the first bar on the left side of the histogram represents all samples with TOC between 0.0−0.1 wt.%, while the second bar represents all samples with TOC between 0.1−0.2 wt.% and so on. Color codes correspond to TOC designations shown for generative potential (quantity of organic matter) in Table 2.

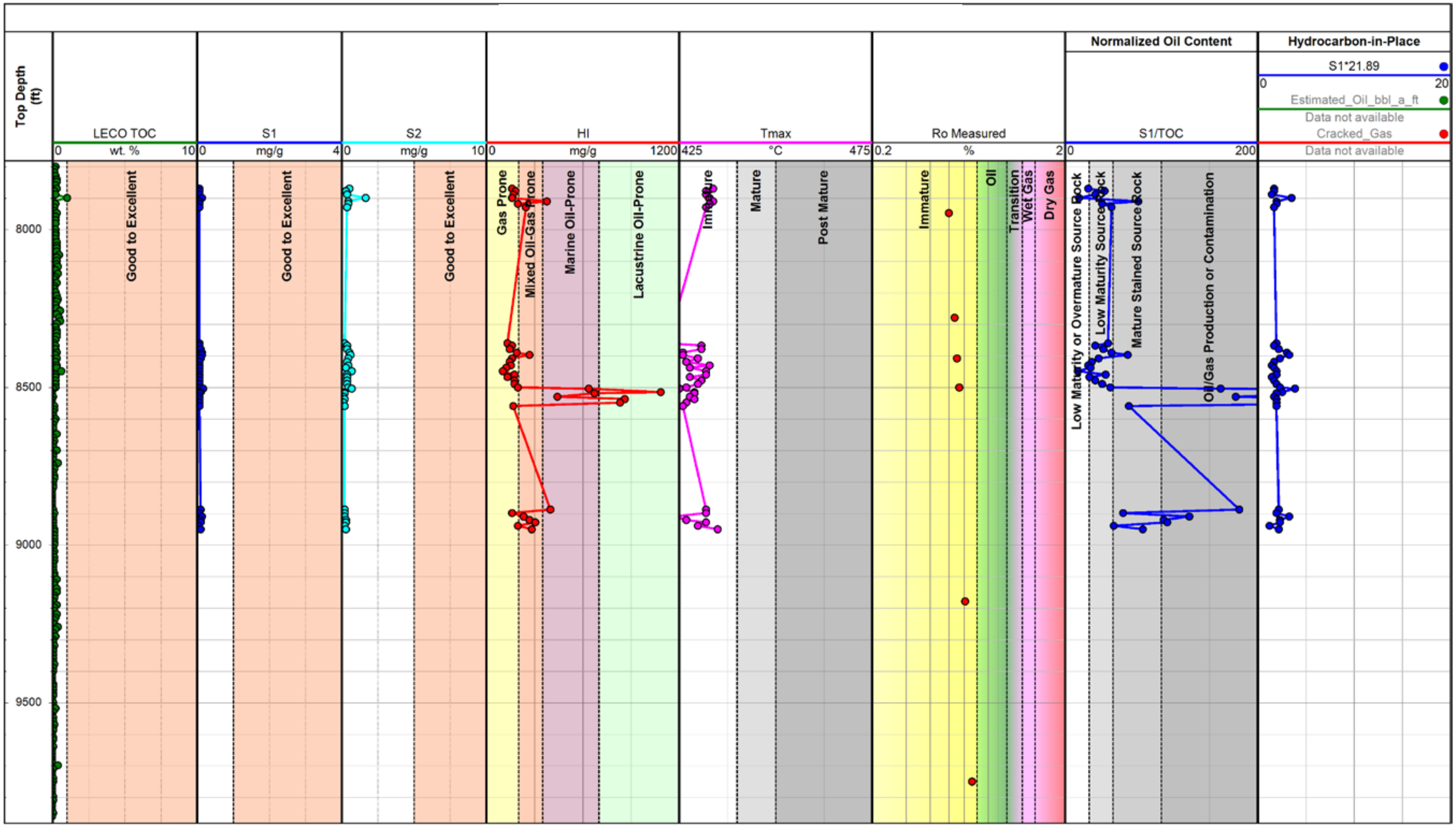

Figure 2.Geochemical depth plots for the Esso #1 well. Note that some Tmax and NOC values plot off scale.

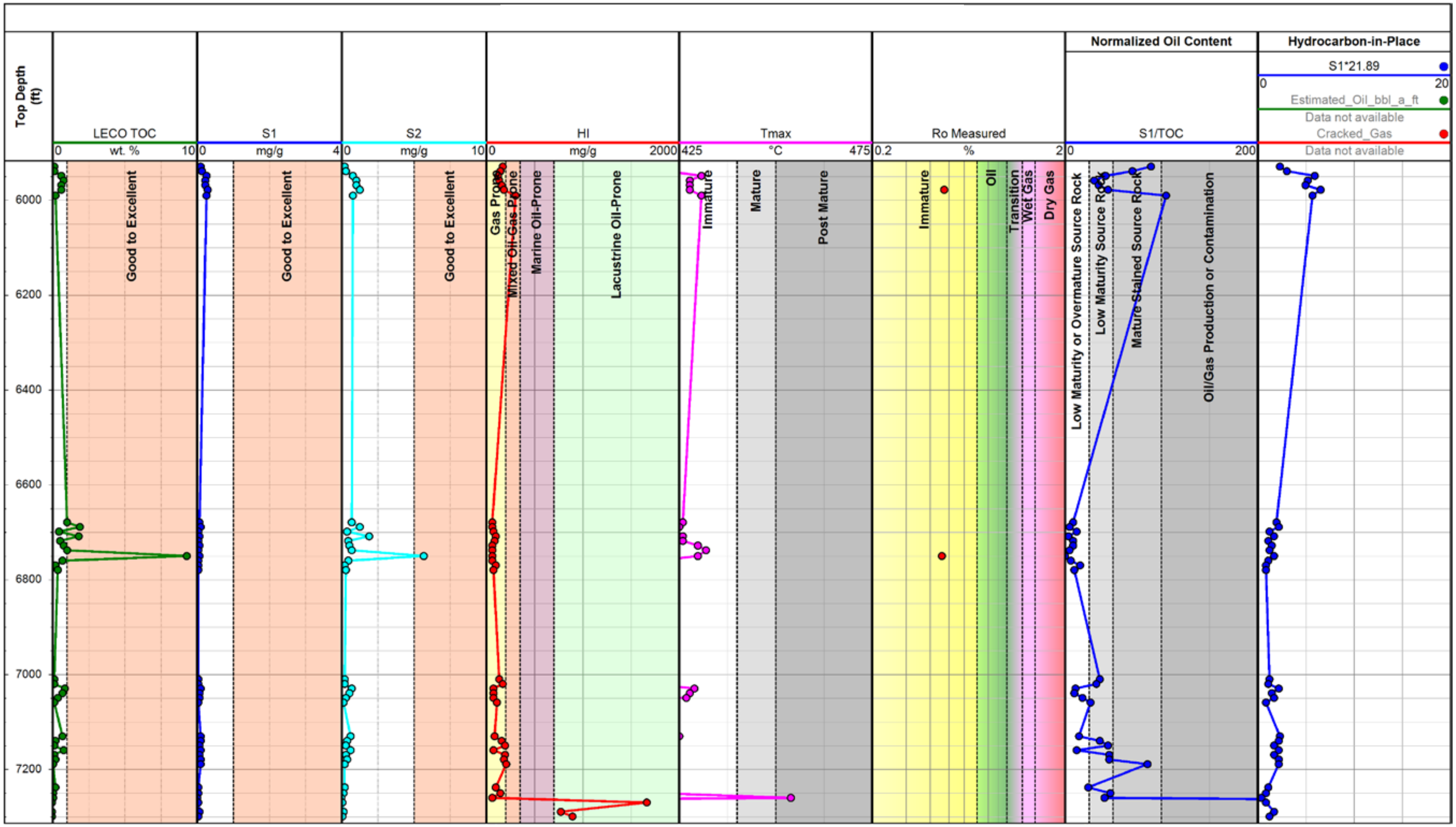

Figure 3.Geochemical depth plots for the Mobil #3 well. Note that some Tmax and NOC values plot off scale.

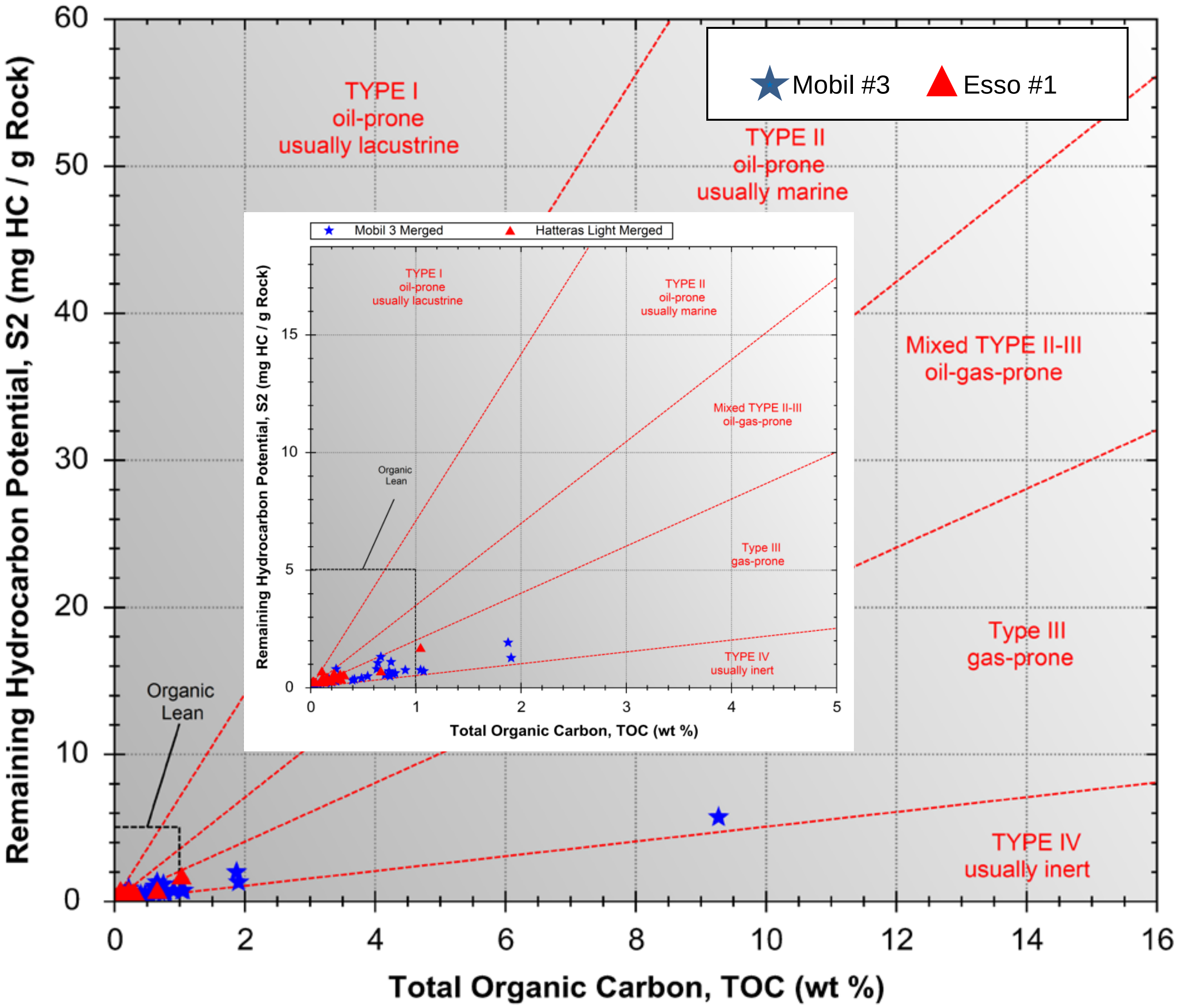

Figure 4.TOC versus remaining hydrocarbon generation potential (S2) for all Lower Cretaceous samples from the Esso #1 and Mobil #3 wells analyzed in the current investigation. Insert graph shows enhanced view of samples which plot in the Organic Lean box.

petrologist did note the occurrence of rare, large, fair quality coaly particles with some appearing to be comprised of rootlets. These may represent caved material due to their relatively large size and thus may be anomalous to the overall trend of TOC within this interval. Most samples from both wells also plot within the box associated with organic lean non-source rocks (Figure 4). The remaining generation potential of these rocks has likely not been reduced to any significant extent due to thermal maturity, as will be discussed in greater detail within following sections of this report.

The normalized oil content, (S1/TOC) X 100, is highly variable in the Lower Cretaceous samples from these wells ranging from 1 to 667 in all samples. A value between 50 and 100 indicates possible oil staining or shows in thermally mature, tight petroleum source rock. Normalized oil contents greater than 100 are usually associated with oil saturated reservoirs. Most of the samples analyzed from the two wells in this study have generally low NOC values (< 50) and these indicate low in-situ hydrocarbon saturation. There are at least two possible causes for high NOC variability in these samples. Some samples have elevated values due to inaccuracies in the measurements, either caused by contamination of the samples or as a consequence of very low TOC content. For example, the highest NOC value of 667 is associated with a sample that only has 0.01 wt. % TOC. In these cases, the NOC values have no statistical validity. The other possible reason some samples have elevated NOC could be due to the occurrence of hydrocarbon filled microfractures, migrabitumen and solid bitumen. Photomicrographs from the Esso #1 well (Figure 5 through Figure 9) appear to show microfractures in different intervals that are filled with either bluish-white fluorescing hydrocarbons (Neogene sample from 810’ depth; 0.30% VRo), yellow fluorescing mobile hydrocarbons (Figure 5), dull orange to brown fluorescing migrabitumen and solid bitumen, which could either represent different hydrocarbon charge events or preferential vertical migration of lighter hydrocarbons from the same charge event. In the Mobil #3 well, orange-brown dead oil fill between mineral grains was also noted in one Lower Cretaceous sample at a depth of 5980’ (Figure 10). Unfortunately, most of the samples examined during organic petrology were not analyzed by programmed pyrolysis and there is no means to confirm the presence of these petrographic observed hydrocarbon features with elevated NOC values. The single sample from the Mobil #3 well at 5980-90’ depth has an NOC of only 45, but the sample immediately below this has an elevated NOC of 106. Further, while the occurrence of hydrocarbon filled microfractures may contribute to the overall S1 yields during programmed pyrolysis (resulting in elevated NOC and PI values), it is still not entirely clear whether such hydrocarbon saturation has originated in-situ or possibly represents the remnants of a hydrocarbon migration event.

Production Index (PI) values in these Lower Cretaceous samples are generally low to moderate (~0.20), but like the NOC values there is some degree of variability. Pyrolysis S1 yields in the both wells average only 0.10 mg HC/g rock or 2 bbl/a-ft (Figure 2 & Figure 3). This suggests a very low amount of in-situ hydrocarbon saturation. Given the generally low hydrocarbon saturations and the sporadic and variable NOC and PI values, it would seem more likely that these are associated with locally generated in-situ bitumen occurrences rather than a wide spread regional migration pathway. However, the geochemical data collected to date is not entirely unequivocal.

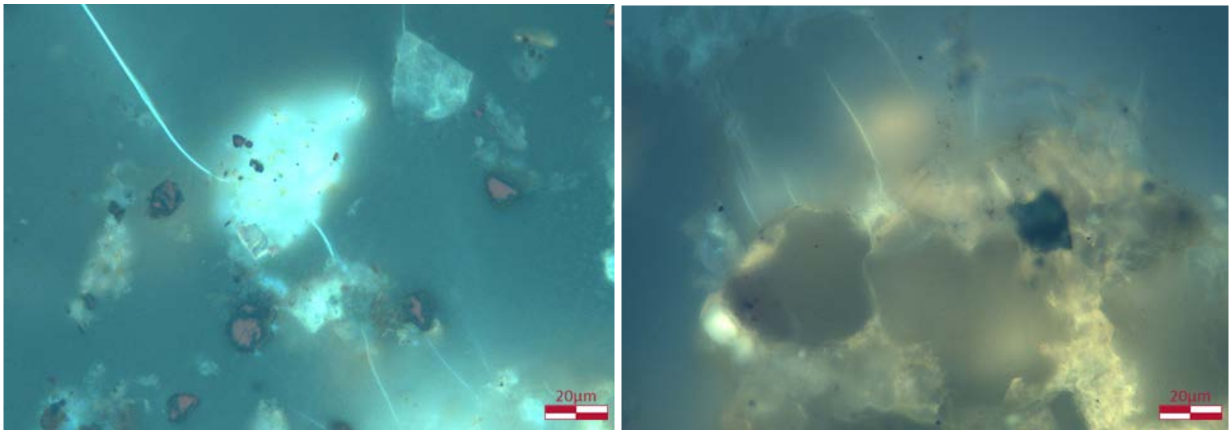

Figure 5.Esso #1 well Sample (Left) 6126520960 (810'): Example of unusual, rare microfractures emanating from mineral matter filled with bluish-white fluorescence, suggesting a possible presence of light hydrocarbons. (Right) Sample 6126520988 (8280'): Example of rare yellow/orange fluorescing mineral matter and surrounding yellow fluorescing microfractures possibly containing mobile hydrocarbons(?).

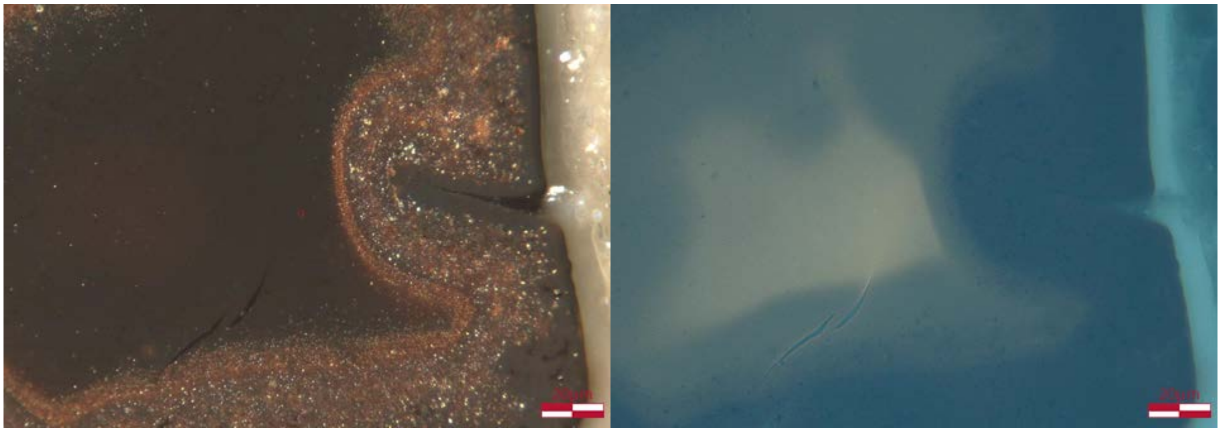

Figure 6.Esso #1 well Sample 6126527253 (7705'): (Left) Large particle of solid bitumen with desiccation cracks. Reflectance from central measuring circle is 0.19% Ro. (Right) Dull orange fluorescence from center of bitumen particle with distinct reductions in intensity moving towards perimeter (possible effects of biodegradation).

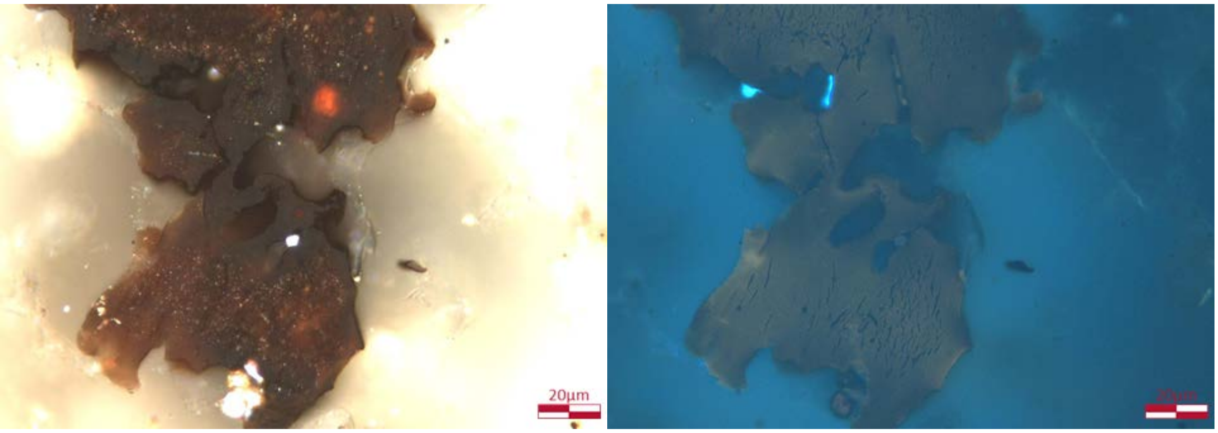

Figure 7.Esso #1 well Sample 6126520986 (7766'): (Left) Solid bitumen with a reflectance reading 0.29%Ro from central measuring circle. (Right) Brown fluorescence from bitumen.

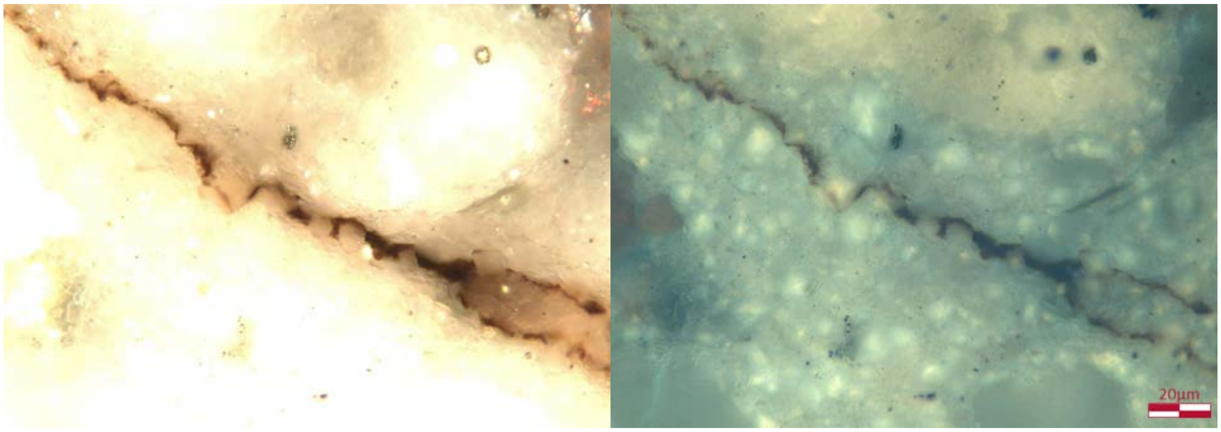

Figure 8.Esso #1 well Sample 6126527257 (7949'): (Left) Migrabitumen filling mineral matrix fracture. (Right) Faint brown fluorescence from migrabitumen and surrounding dull yellow to orange mineral fluorescence.

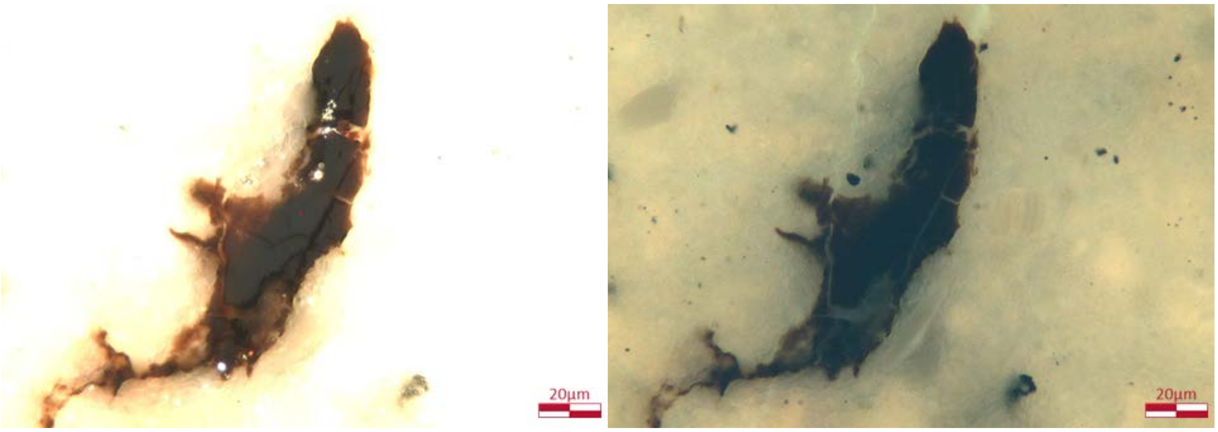

Figure 9.Esso #1 well Sample 6126527259 (8763'): (Left) Potential solid bitumen particle. Reflectance reading not possible due light intensity elevation from surrounding mineral matrix. (Right) Weak brown fluorescence from perimeter of solid bitumen.

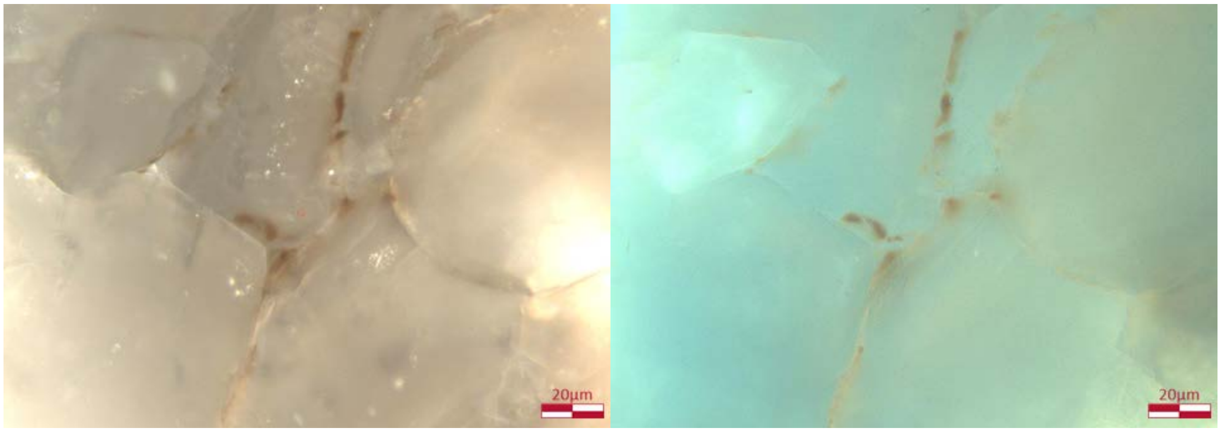

Figure 10.Mobil #3 well Sample 6126563870 (5980'): (Left) Possible brown dead oil trapped between mineral grains. N.B. This was the only observation of this type in the sample. (Right) Under UV light the dead oil(?) exhibits dull orangey-brown fluorescence.

KEROGEN TYPE AND EXPELLED PRODUCT

The organic matter in the Lower Cretaceous rocks in these wells appears to be a combination of oil-prone marine algal material, gas-prone terrigenous organic matter, and variable amounts of oxidized/reworked organic material. These rocks would be expected to generate minor volumes of both oil and gas at peak maturity. Measured Hydrogen Index (HI) values in the Lower Cretaceous samples from the Esso #1 well range from 105−1086 mg HC/g TOC and average 293 mg HC/g TOC (Figure 11). In the Mobil #3 well the measured HI values range from 61−1667 mg HC/g TOC and average 204 mg HC/g TOC (Figure 11). Some of the lowest TOC samples have very elevated HI values > 1000 mg HC/g TOC and these are not considered reliable due to probable inaccuracies in the measurements. Another possible explanation for these elevated HI values is a consequence of in-situ oil/bitumen, since hydrogen-rich hydrocarbons can contribute to the S2 peak and result in anomalously elevated HI ratios. One method to overcome this artifact is to perform solvent extraction on select samples and re-analyze them by TOC and programmed pyrolysis (this was not done in the current study). Kerogen HI values in these samples have not likely been reduced to any extent due to thermal maturity, and they indicate mixed oil/gas-prone Type II/III to gas-prone Type III kerogen quality in these rocks at present day. Most of the samples analyzed from these two wells contain very elevated Oxygen Index (OI) values, which are even outside the typical plotting diagram (Figure 11). This could be due to the presence of oxidized organic matter (Figure 12). It should be noted that OI values in carbonate sequences can be adversely influenced by the presence of low temperature decomposing carbonate minerals like siderite and thus should be interpreted with caution.

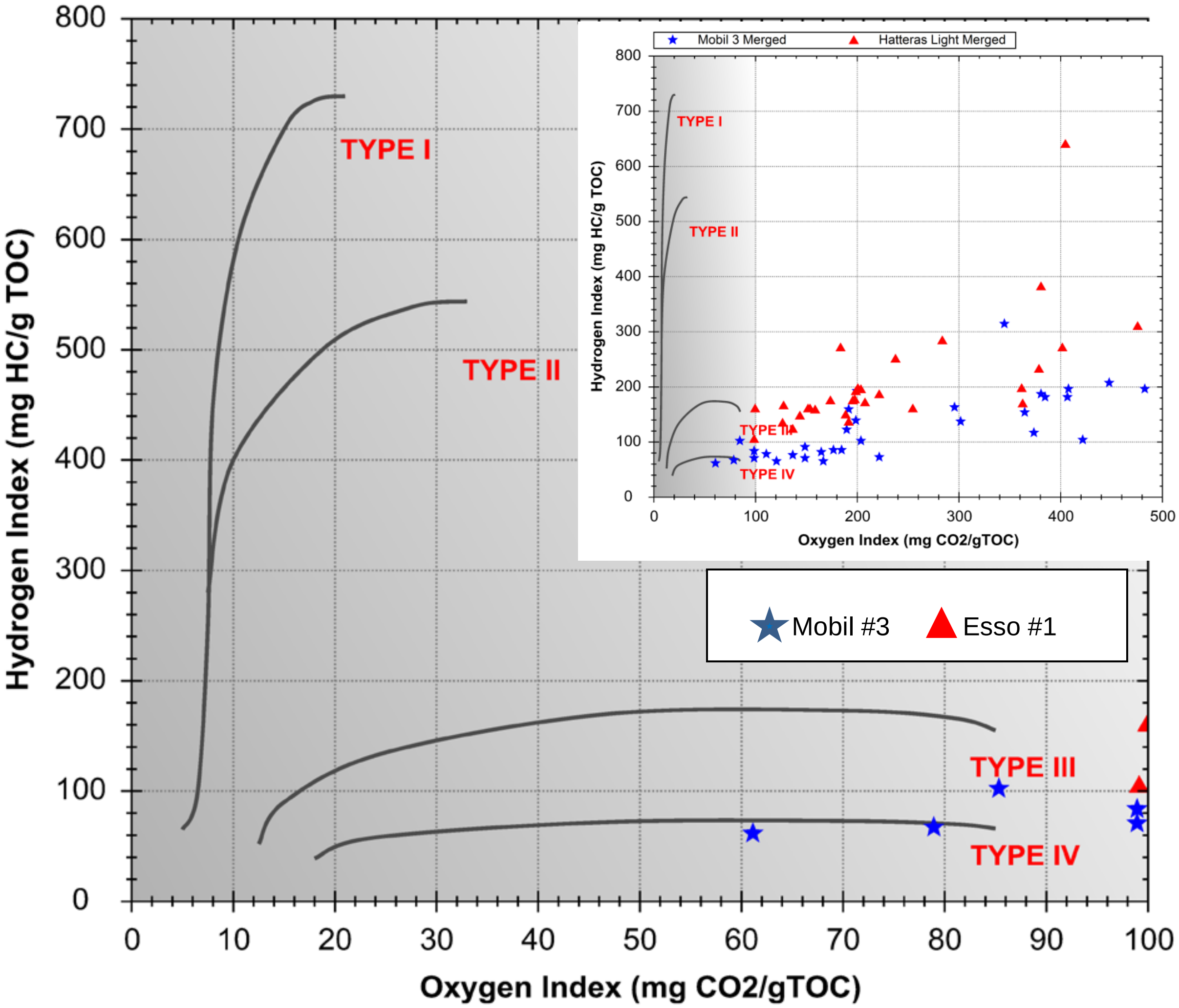

Figure 11.HI versus OI plot of the Lower Cretaceous samples from the two wells examined in the current investigation (insert diagram shows expanded OI scale). Most samples plot in the gas-prone Type III region, but others appear to represent a mixture with oil-prone algal Type II kerogen and degraded/oxidized Type IV kerogen.

Organic petrology results confirm that the Lower Cretaceous rock samples from both wells examined in the current study contain a mixture of organic matter types. In most samples there are rare occurrences of oil-prone Type II kerogen dominated by diffuse amorphous organic matter (AOM), along with cutinite and resinite. Minor amounts of oil-prone Type I structured marine algal liptinite are also noted (Figure 12). The relative proportions of algal debris vary from sample to sample and algal fluorescence colors range from yellow to orange, which may be a consequence of differential reworking prior to preservation (Figure 12). In addition to oil-prone organic matter, rare oxidized, inert Type IV organic matter and well preserved Type III vitrinite were also found in variable amounts during organic maceral analyses (Figure 12). Vitrinite macerals were observed in the form of collotelinite (representative vitrinite for Ro measurements), collodetrinite (hydrogen-rich form of vitrinite that produces marginally lower Ro measurements than collotelinite) and oxidized/reworked vitrinite (elevated Ro measurements). All of these observations are consistent with non-source rocks deposited in a fairly oxidizing marine depositional environment that contains input of transported terrigenous organic material mixed with minor amounts of marine organic matter.

Although highly variable, the average maceral composition of all Lower Cretaceous samples from the Esso #1 well was calculated to contain 27% Type I, 7% Type II, 32% Type III and 33% Type IV kerogen macerals. Only two samples were examined from the Mobil #3 well and the average maceral composition was 22% Type I, 11% Type II, 54% Type III and 13% Type IV kerogen macerals. Note that this determination does not take into account the variable and sporadic occurrences of solid bitumen within these samples. Furthermore, it should be noted that maceral concentrations are extremely low with the majority of components present in area percentage amounts <1% (whole rock basis).

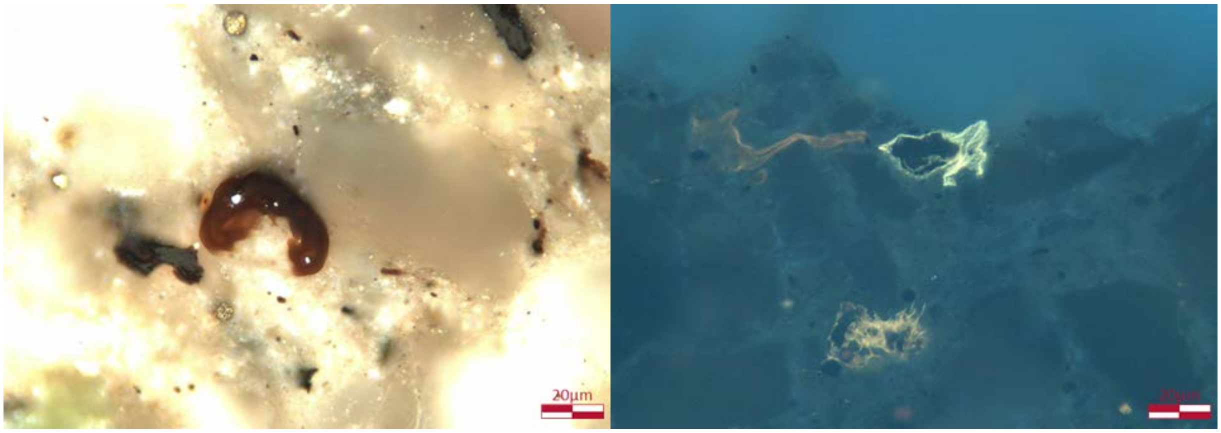

Figure 12.Esso #1 well Sample 6126527251 (7503'): (Left) Reworked, brown spore (center) and vitrinite particle to left with a reflectance value of 0.50%Ro. (Right) '): Varicoloured fluorescing algal debris within same rock particle ranging from yellow (autochthonous), through yellow/orange to orange (reworked/allochthonous?).

THERMAL MATURITY

The organic-matter in the Lower Cretaceous formations in both of the wells evaluated in the current investigation appears to be thermally immature with respect to the oil generation window. Pyrolysis T_{max} values average 416˚ in the Mobil #3 well and 430˚C in the Esso #1 well, which indicates that the organic matter is immature with regard to oil generation for mixed Type II/III kerogen (Figure 13). Typical Type II kerogen enters the early oil window at Tmax values > 435˚C. Using the formula published by Drozd and Knowles (2016) for Type II kerogen (Calculated Ro = (0.0181)(Tmax) – 7.147), the average measured Tmax values of 416 & 430°C are equivalent to Calc. %Ro values of 0.38 & 0.64%, respectively. It is important to note that Tmax is only a crude measure of thermal maturation (Peters, 1986) and it can be compromised by a variety of pyrolysis artifacts and caveats, including the presence of low-temperature S2 shoulders in samples with elevated in-situ oil saturation and inaccurate/spurious readings in samples with very low S2 yields.

As noted previously, NOC and Production Index (PI) values for the samples analyzed in this study are highly variable. The PI values are mostly in the early mature range of ~0.10 to 0.20 (Figure 14), although there are many higher values (up to 0.40) that would normally indicate elevated in-situ hydrocarbon saturation and more thermally mature organic matter. Pyrolysis S1 yields in the both wells average only 0.10 mg HC/g rock or 2 bbl/a-ft (Figure 2 & Figure 3). This suggests a very low amount of in-situ hydrocarbon saturation. Thus, the elevated PI values are more likely indicating hydrocarbon staining and/or contamination and fall within the region of the plot generally associated with this artifact (Figure 14). This could be interpreted as supporting evidence for the occurrence of a migrated oil stain within these samples.

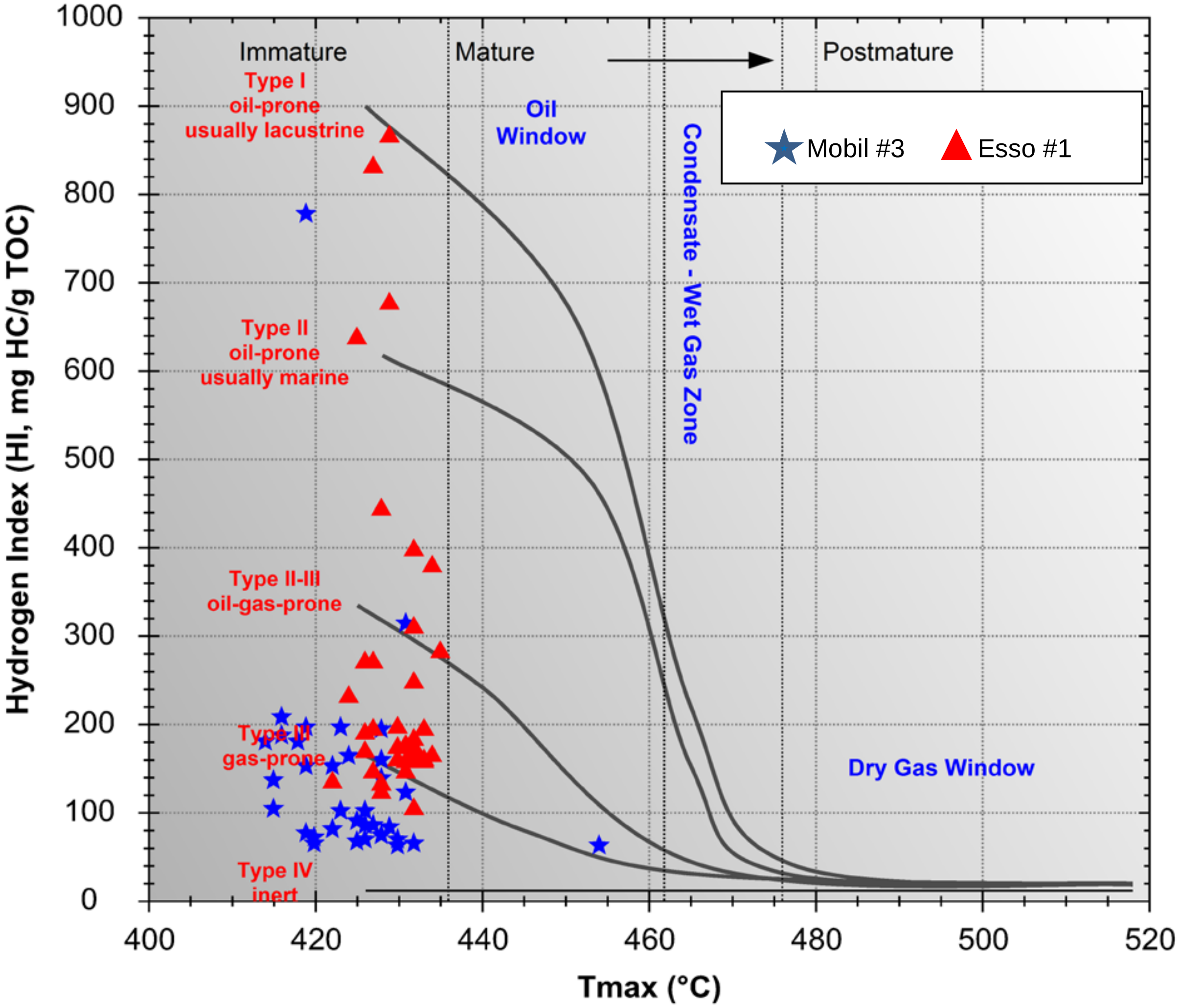

Figure 13.Hydrogen Index (HI) versus T_{max} plot of the Lower Cretaceous samples from the two wells examined in the current investigation. Samples with T_{max} <435 ˚C are immature.

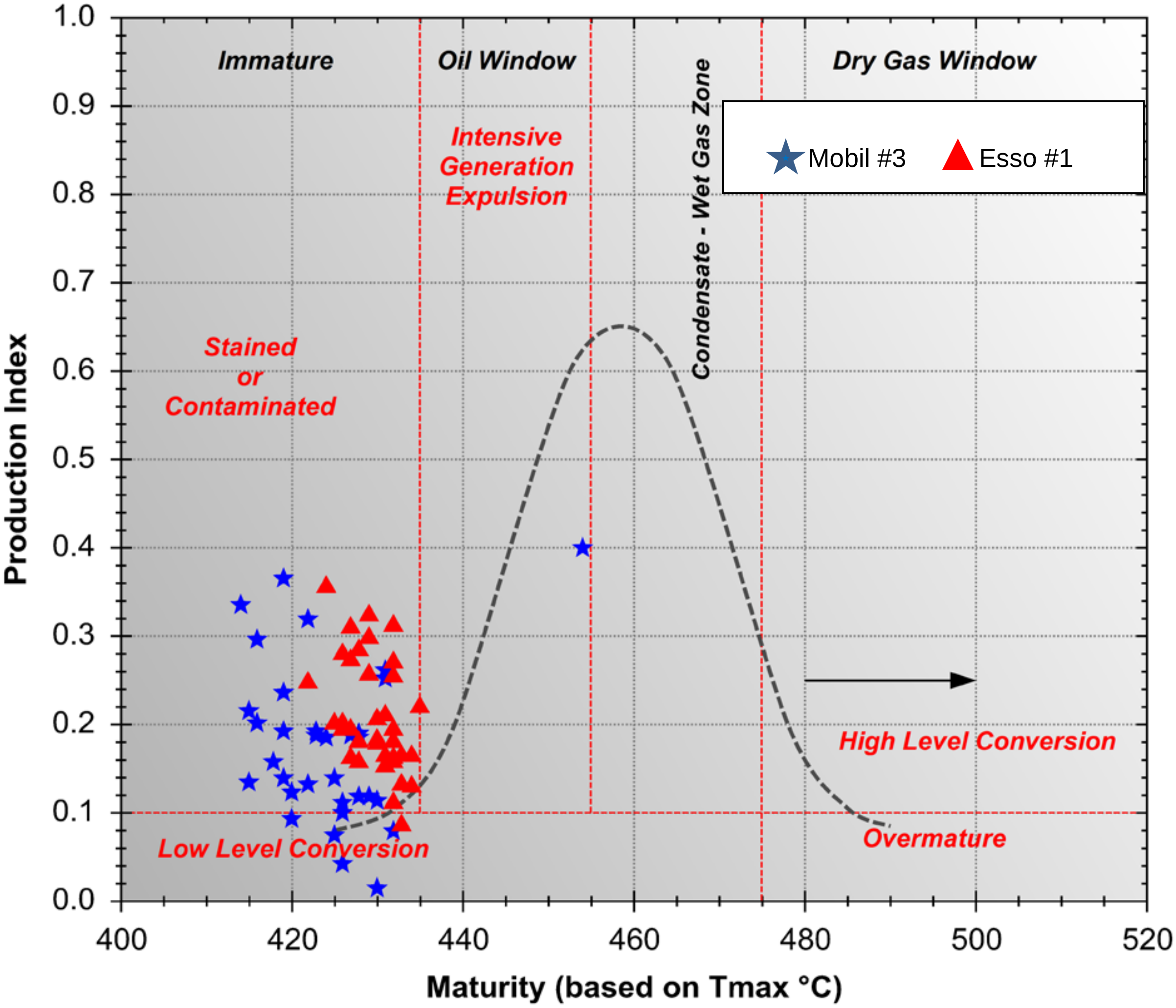

Figure 14.Production Index (PI) versus T_{max} plot of the Lower Cretaceous samples from the two wells examined in the current investigation. Trend envelop shown by dashed line is based on WFT Labs analysis of over 5000 shale samples.

Attempts were made to estimate kerogen transformation ratios (TR) for the Lower Cretaceous samples on the basis of estimated original and measured present day HI values using the approach outlined in Jarvie et al. (2007). Unfortunately, few samples (2 from each well) were available in which kerogen maceral determinations and programmed pyrolysis were both performed on the same sample depth. In these samples the estimated TR range from 47-66% in the Esso #1 well to 39–90% in the Mobil #3 well. These values are not considered reliable and this methodology is prone to significant potential error when applied to immature samples.

Measured vitrinite reflectance analyses were attempted on a total of 25 samples (Esso #1 – 23; Mobil #3 – 2), but due to the low organic carbon content and the lack of good quality vitrinite, reliable readings were not obtained on all samples. In the Esso #1 well the total number of vitrinite reflectance readings per sample was < 20 and the vitrinite quality and confidence is generally considered fair to poor. In the two samples analyzed from the Mobil #3 well, only one sample had a statistically confident number of readings (50) and was considered to be good quality. Most samples contained a significant population of both reworked and oxidized vitrinite (which have higher reflectance than indigenous collotelinite) and some also had a population of collodetrinite (which has lower reflectance than indigenous collotelinite). It is likely that episodic euxinic conditions in the shallow marine depocenter and lengthy transport for woody organic matter are both responsible for the high relative abundance of oxidized and reworked material. It is also possible that these oxidized and reworked macerals could have originated from uplifted and eroded Triassic rift basin sediments to the west.

In the Esso #1 well, mean vitrinite reflectance (VR) values range from 0.30% VRo at 810' to 0.66% VRo at 9750'. Liptinite fluorescence colors tend to show good agreement with the VR data with autochthonous material exhibiting yellow fluorescence, suggesting a maturity estimate of 0.4-0.6% VR/e. Reworked liptinite tended to show darker orange to light brown fluorescence, suggesting a higher maturity estimate of 0.7-1.0% VR/e. Possible, tentative, occurrences of mobile hydrocarbons were noted in samples at 815' that contained rare occurrences of microfractures radiating from mineral matter filled with bluish-white fluorescence (light hydrocarbons?) and the sample at 8280' that contained yellow/orange fluorescing mineral matter with surrounding yellow fluorescing microfractures (Figure 5).

In a study of fluorescence colors in fluid inclusions, George et al. (2001) noted that although the relationship between API gravity and the fluorescence properties of crude oil is well established, the extension of this to the use of fluorescence colors of oil inclusions as a qualitative thermal maturity guide is not justified. Samples with mainly yellow and orange fluorescing oil inclusions tend to have maturities in the lower half of the oil window. However, the authors strongly caution against the widespread application of the paradigm that blue fluorescent oil inclusions indicate high maturity oil. Detailed molecular geochemical data show that samples containing dominantly blue fluorescing oil inclusions can have considerable variability in chemical composition caused by source, biodegradation and maturity (George et al, 2001). Thus, for the samples examined in the current study the occurrence of blue/white fluorescing hydrocarbon microfractures in the Esso #1 well at a depth of 815’ do not unequivocally indicate the presence of a high maturity migrated oil charge. Likewise, the occurrence of yellow fluorescing microfractures in the Lower Cretaceous sample at a depth of 8280’ is entirely consistent with local generation of low maturity bitumen from organic matter at low thermal maturity (< 0.65% Ro; George et al., 2001).

Very rare occurrences of solid bitumen and migrabitumen were noted in samples at 7705', 7766', 7949' and 8763' (Figure 6 through Figure 9). Solid bitumen reflectance readings in the sample at 7771’ average 0.28% BRo. Using the formula published by Ruble et al., (2016) following Knowles (2016), the resultant Eq. Ro value of 0.58% VR/e would place the Lower Cretaceous interval in the immature window and is consistent with other measured maturity parameters.

In the Mobil #3 well, the sample at 5980' has a mean vitrinite reflectance (VR) value of 0.47% VRo based on 50 measurements. The sample at 6750' has a mean value of 0.46% VRo but based on only 12 measurements. It is possible that this value may be related to caved coaly particles. Rare to few occurrences of yellow fluorescing filamentous algae and algal debris are also present, suggesting a maturity estimation of 0.4-0.6% VR/e. A single observation of possible trapped dead oil in mineral fractures that exhibits weak orange fluorescence under UV light was noted in the sample from 5980' (Figure 10). Weak yellow mineral fluorescence was also common in the same sample.

The organic petrology data collected in the current investigation was considered sufficient to constrain a thermal maturity depth profile (Figure 15). A logarithmic regression line based on all Esso #1 well samples containing representative vitrinite produce a trend that suggests onset of oil generation window (0.6% VRo) occurs at approximately 9200'. Thus, the entire Lower Cretaceous interval in this well would be considered to be immature with regard to the oil window (but not the bitumen generation window as described below). Only the underlying sections (> 9100’ depth) appear to have entered into the early oil window on the basis of this interpreted thermal maturity depth trend. This is consistent with the majority of the geochemical maturity data evaluated in this study.

Client supplied data collected from a separate organic petrology investigation (M. Malinconico, per. comm., 2017) was provided and compared against the data collected in the current study. In general, the data from the previous investigation was ~0.05% VRo lower in comparison to the data from the current study (Figure 15). Both data sets generate similar trend lines that are offset from each other by the same magnitude throughout the entire depth range. The causes for this disparity are unknown and have not been thoroughly investigated. In the present study, several occurrences of collodetrinite, the hydrogen-rich and slightly lower reflecting form of vitrinite, were noted. If one observes small particles of collodetrinite in the absence of any supporting evidence such as presence of embedded liptinite, it could be possible to incorporate readings from this material in with those from collotelinite (the representative form). In general, collodetrinite reflectance on average is approximately 0.1% VRo lower than that of collotelinite over the range from immature to end oil window. Thus, if a few readings from this material were potentially incorporated with collotelinite readings in the client supplied data study, then it is possible that the overall average VRo would be slightly lower. A detailed statistical evaluation of the histogram data from both studies might offer further insights.

Lewan (1997) described the processes thought to occur during hydrocarbon generation in both nature and in hydrous pyrolysis laboratory simulation experiments. These processes happen in three stages: (1) bitumen generation, (2) immiscible oil generation, and (3) pyrobitumen/gas generation. Kerogen decomposition to bitumen involves cleavage of weak noncovalent bonds at low maturity, producing a substance enriched in high molecular-weight hydrocarbons and heteroatom components (Lewan, 1993). At higher maturity, the bitumen that is saturated with dissolved water undergoes partial decomposition, producing aliphatic moieties that form an immiscible oil phase (Lewan, 1994). This immiscible oil phase is expelled from the source rock during primary migration and is collected from the surface of the water at the completion of each hydrous pyrolysis experiment. In natural systems, this expelled oil travels out of the source rock into adjacent carrier beds and moves upward to more shallow depths due to buoyancy effects. At higher maturity, the expelled oil and retained bitumen eventually decomposes into gas and pyrobitumen (Lewan, 1993). For the two wells examined in the current study, geochemical thermal maturity data suggest that they are immature with regard to the main oil generation window, but likely have achieved sufficient thermal maturity to have entered the main bitumen generation window. Thus, solid hydrocarbon occurrences found during organic petrology could possibly represent in-situ generated bitumen. Alternatively, the disperse nature of the occurrences of these solid hydrocarbons could indicate an origin from expelled oil along a paleo-migration pathway.

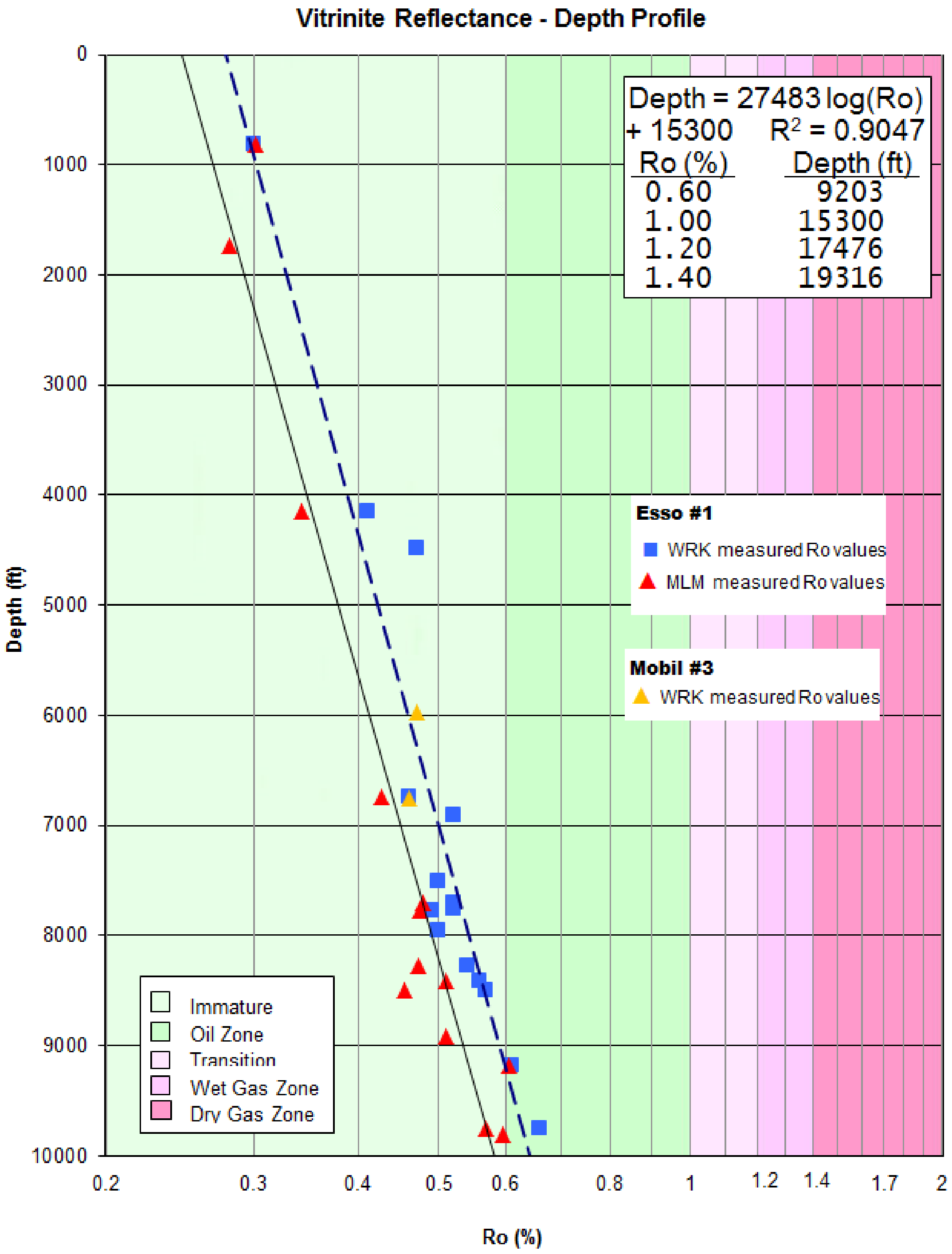

Figure 15.Thermal maturation based on measured vitrinite reflectance (%VR$_o$) versus depth for the samples examined in this study (noted by petrologist initials as WRK data). Data is also shown for client supplied vitrinite reflectance on samples from the Esso #1 well (noted by petrologist initials as MLM data). The dashed trend line incorporates WRK data for the Hattras Light well, while the solid trend line is for the MLM data set. The two samples from the Mobil #3 well are shown against these trend lines and were not incorproated into the calculated trends.

GAS CHROMATOGRAPHY FINGERPRINT & BIOMARKERS

Due to limited sample quantities, two (2) cuttings composites from the Lower Cretaceous intervals in the Esso #1 (7800-8130') and Mobil #3 (5930-7309') wells were solvent extracted and analyzed by gas chromatography (GC). In addition, solvent extracts were fractionated by medium pressure liquid chromatography (MPLC) and the saturate and aromatic fractions were analyzed by gas chromatography mass spectrometry (GC-MS) for biomarker analysis.

A cross plot of the soxhlet extractable organic matter (EOM) versus the volatile hydrocarbon S1 yield (Figure 16) was prepared to examine in-situ hydrocarbon saturation in these samples. This plot indicates that in-situ hydrocarbon saturation as measured by solvent extraction is slightly greater than volatile hydrocarbon saturation. Both samples would be considered to have poor volatile hydrocarbon saturation (S1 < 0.5 mg HC/g rock). However, the solvent extractable saturations are considered fair (bitumen 500-1000 ppm). The slightly elevated EOM content in both samples is more indicative of “bitumen” saturation rather than volatile, mobile “oil” saturation. This observation is consistent with the interpretation that Lower Cretaceous rocks in both wells examined in this study are immature with regard to the main oil generation window. However, given the age of these cuttings samples (> 50 years old) and their storage in unairconditioned facilities, the loss of volatile components is not unexpected and does not necessarily rule out the presence of an original migrated oil signature that might have contained a greater abundance of volatile components.

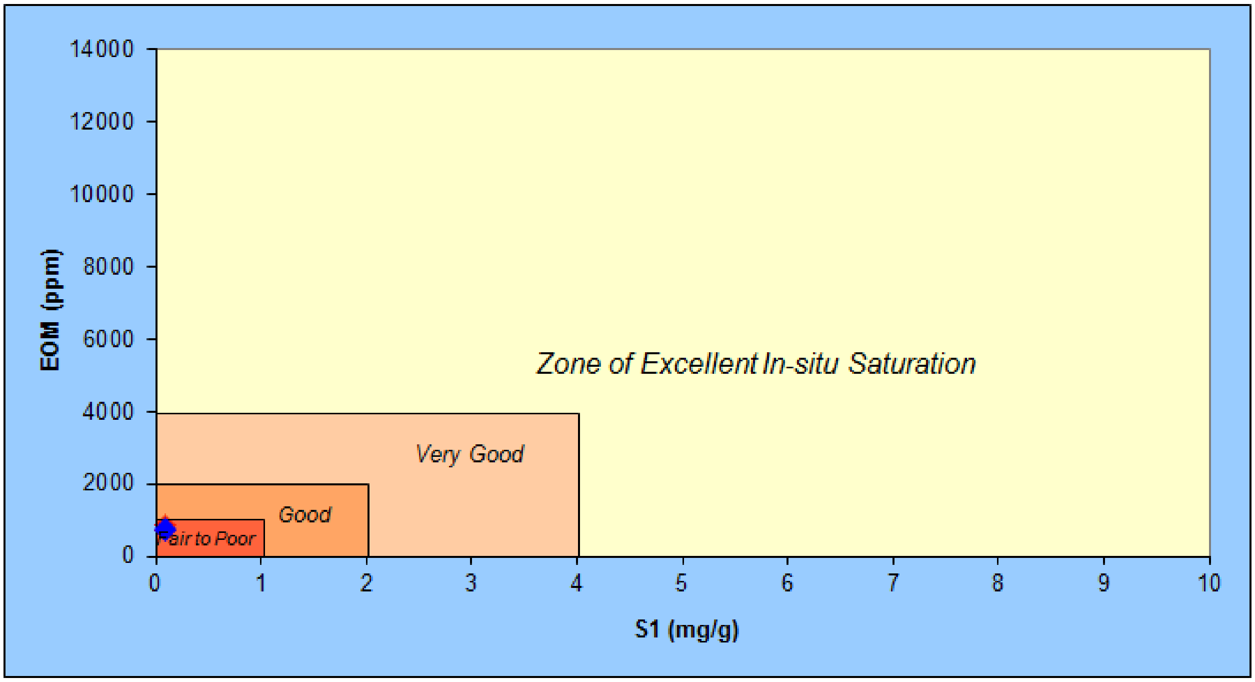

Figure 16.Cross plot of extractable organic matter (EOM) versus programmed pyrolysis volatile hydrocarbon S1 yields from composite cuttings samples in the Esso #1 (red symbol) and Mobil #3 (blue symbol) wells.

Esso #1 Rock Extract

The bulk fractional composition of the Lower Cretaceous rock extract (7800-8130’) from the Esso #1 well (Figure 17) is composed of predominantly polar nitrogen, sulfur and oxygen (NSO) compounds (70%), with lower abundances of saturates (22%), aromatics (4%) and asphaltenes (3%). This is fairly common in immature samples that may contain a high abundance of organic acids, but could also be an artifact of contamination. The GC fingerprint is generally characterized by dominant contamination peaks likely associated with phthalate plasticizer components (Figure 17). The subordinate normal alkane envelope is unimodal with maxima in the C16 – C17 range. Carbon Preference Index (CPI) value is 1.30, indicating a strong odd carbon predominance that is fairly typical of marine shales and an extract that is thermally immature (Peters et al., 2005). The ratio of pristine/phytane (Pr/Ph) is near unity at 1.04, which offers minimal insights into paleoenvironmental redox conditions during deposition. This extract also has relatively low aromatic sulfur biomarkers as indicated by dibenzothiophene/phenanthrene (DBT/Phen) ratio of 0.03, which is also typical of marine shale lithologies. A cross-plot of the Pr/Ph ratio versus the DBT/Phen ratio place the Esso #1 extract within the zone designated for marine and lacustrine shales (Figure 19).

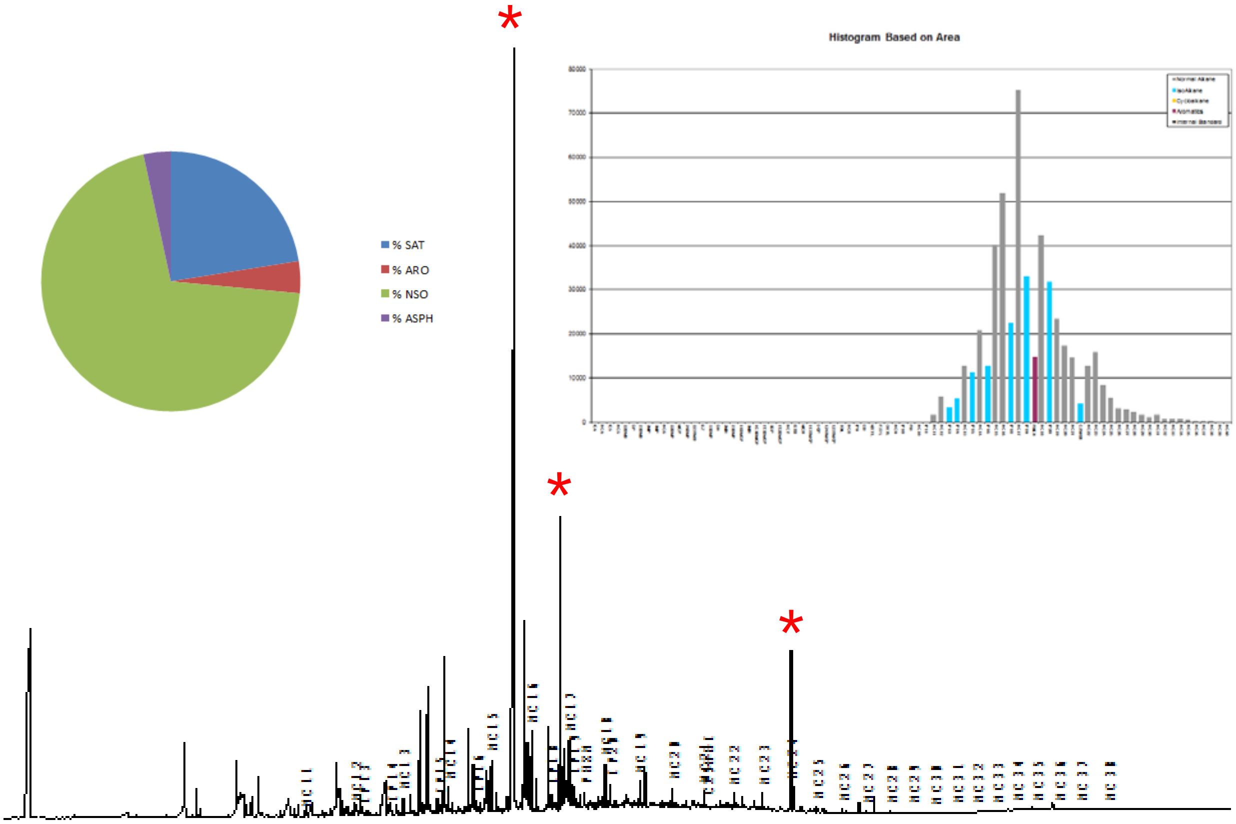

Figure 17.Solvent extract gas chromatogram of a Lower Cretaceous composite sample from the Esso #1 well (7800-8130’). Insert pie diagram shows MPLC fractional composition of rock extract and histogram of alkanes (grey), isoprenoids (light blue) and aromatics (magenta). Peaks noted with red asterisk symbols are probable contaminants.

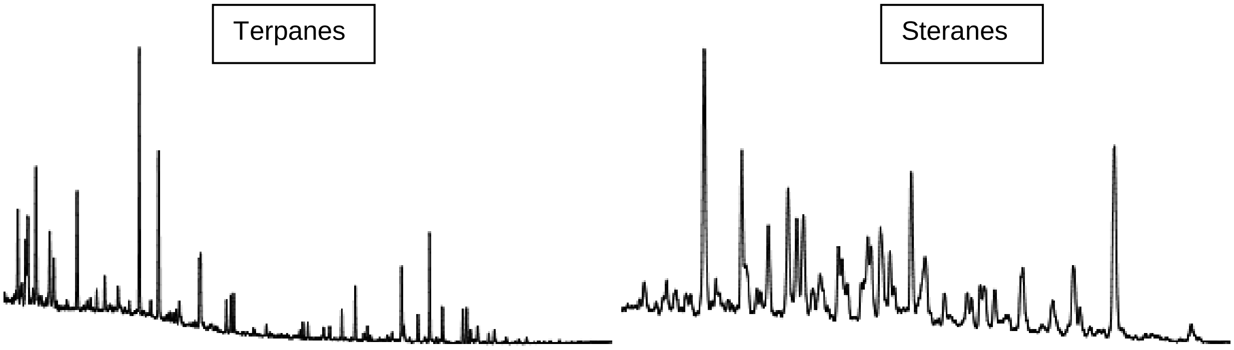

Figure 18. Biomarker mass fragmentograms from the saturate fraction of the Lower Cretaceous composite sample from the Esso #1 well (7800-8130'). The m/z 191 fragmentogram on the left illustrates the tri- and pentacyclic terpanes, while the m/z 217 fragmentogram on the right illustrates the diasteranes and steranes.

Biomarker data show other characteristic features common to marine shales. There is a very high abundance of tricyclic terpanes (Figure 18) and the ratio of Tricyclic terpane/Hopanes is 2.55. The hopane distributions are dominated by C30 hopane, with lesser abundances of the C29 hopane (Figure 18). The relative distribution of various tricyclic terpane and hopane ratios can be used to further distinguish depositional environment and source rock lithology (Figure 20) In these plots, the Esso #1 rock extract appears to plot in areas generally interpreted to be representative of marine shale source rocks, although there is overlap with the carbonate regions. This interpretation is somewhat inconsistent with the dominant carbonate lithology of this specific depth interval (7800-8130') in the Hatteras Well as determined by log response (J. Reid, per. comm.). However, most of the overlying and adjacent Lower Cretaceous rocks in this well are shale dominated and thus any in-situ generated hydrocarbon signatures may be more reflective of these zones as potential source rocks (versus the interbedded sands and carbonates).

Biomarker data can also be used to age-date oils and rock extracts and one particularly useful plot for this purpose is illustrated in Figure 21. Oleanane is generally thought to be a Cretaceous or younger higher plant biomarker that is probably derived from betulins, taraxerene and other pentacyclic triterpanes in angiosperm flowering land plants (Peters et al., 2005). Angiosperms first became predominant in the Late Cretaceous and only rare examples of oleananes have been found in oils known to be older than the Cretaceous (Peters et al., 2005). For the present investigation the detection of oleanane in the rock extracts was considered to be a critical biomarker to evaluate whether the in-situ hydrocarbon signature was indigenous or possibly related to a migrated hydrocarbon charge from an older, deeper source rock (Jurassic?). The Esso #1 extract has a moderately high oleanane/C30 hopane ratio of 0.07 and plots within the region of probable late Cretaceous source rocks (Figure 21). The oleanane ratio is influence by thermal maturity and generally increases from low values in immature rocks to a maximum value at the top of the oil window (Peters et al., 2005). This interpretation can also be complicated by the presence of two isomers of oleanane, with the 18β (H)-oleanane found in immature bitumens and the more thermally stable 18α (H)-oleanane found in oils. In the present study the reported oleanane/hopane ratio incorporates both isomers for calculation purposes to avoid these complications. Oleanane is considered a marker for both geologic age and source input, with higher abundances associated with greater higher plant input. The C30-sterane index in the cross-plot shown in Figure 21 generally increases with marine versus terrigenous organic-matter input into the source rock. For the Esso #1 extract, the C30-sterane index value of 2.4 is fairly low, which would suggest significant terrigenous input. This biomarker data is in general agreement with organic petrology evidence showing a mixed kerogen maceral assemblage with on average 32% Type III kerogen composition in the Lower Cretaceous interval within the Esso #1 well.

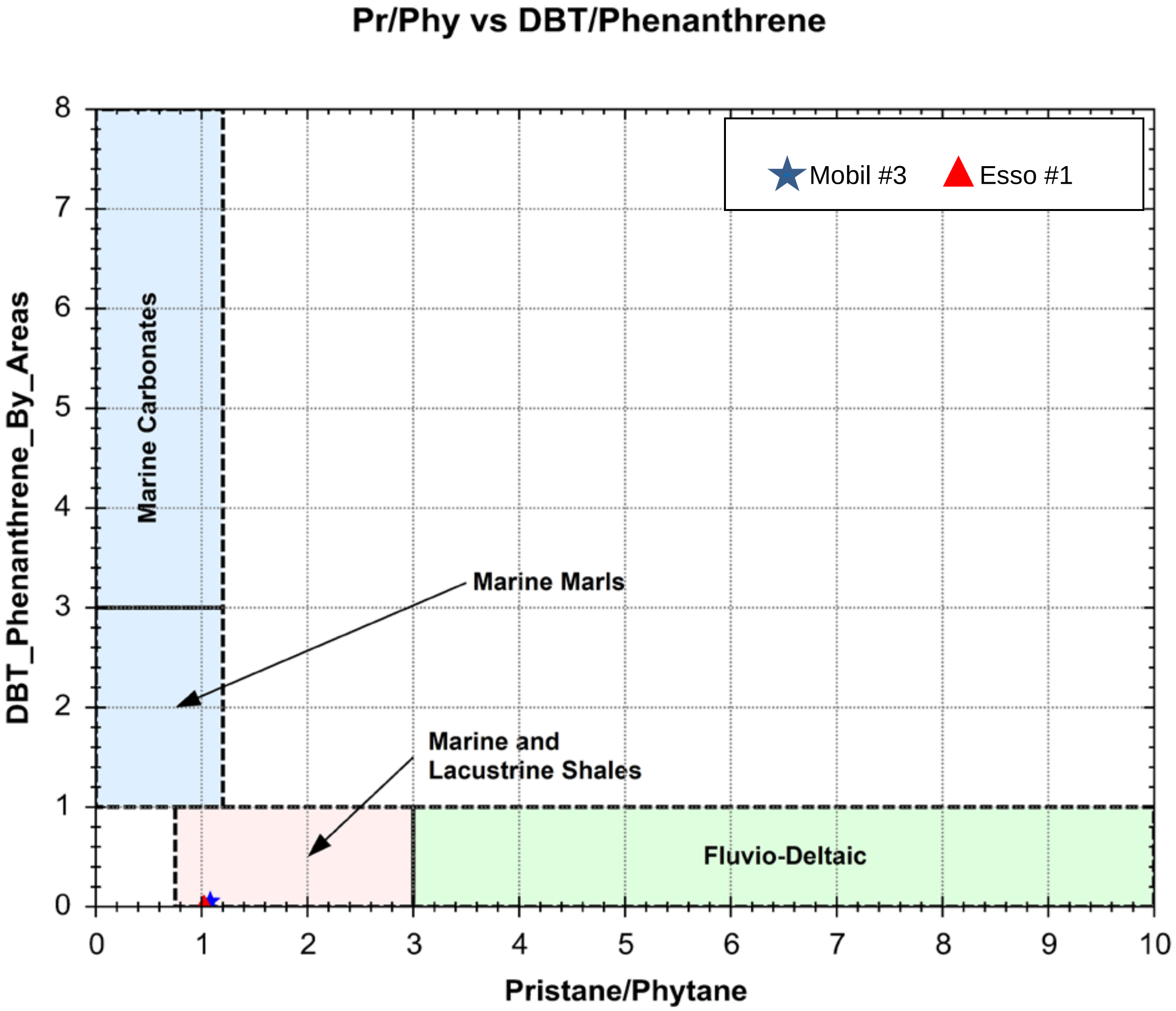

Figure 19**.The ratio of dibenzothiophene to phenanthrene can be used to determine if the oil source rock was shale or a carbonate. Pristane/phytane data allow fluvio-deltaic source rocks to be distinguished from marine and lacustrine shales. Therefore, a cross-plot of these parameters allows the depositional environment of an oil source rock to be deduced (Hughes et al., 1995).**

Gammacerane, which is a biomarker dominant in saline lacustrine source rocks, is present in minor amounts in both samples analyzed in the current study. A cross plot of Gammacerane/Hopane versus the C35/C34 Homohopane ratio (Figure 22) has been used to distinguish the Lower Cretaceous extracts in terms of their probable depositional environment. The presence of high abundances of gammacerane in oils and extracts indicates a stratified water column or hypersaline conditions in marine and non-marine source rocks. The relatively low Gammacerane/Hopane ratio of 0.13 in the Esso #1 extract would imply fluctuating euxinic conditions within the marine depositional setting and this sample plots in the region of the diagram associated with marine-deltaic-paralic source rocks (Figure 22). The C35/C34 homohopane ratio has been shown to differentiate rock extracts and oils from different depositional environments (Figure 22). In marine kerogens, high C35/C24 homohopane ratios suggest oil-prone rocks deposited in reducing environments and low ratios suggest more gas-prone kerogens deposited in oxidizing environments. The Esso #1 extract has a C35/C34 homohopane ratio of 0.67 and plots in the region of more oxidizing depositional environment which is generally consistent with the low preservation of organic matter in these Lower Cretaceous rocks in this well.

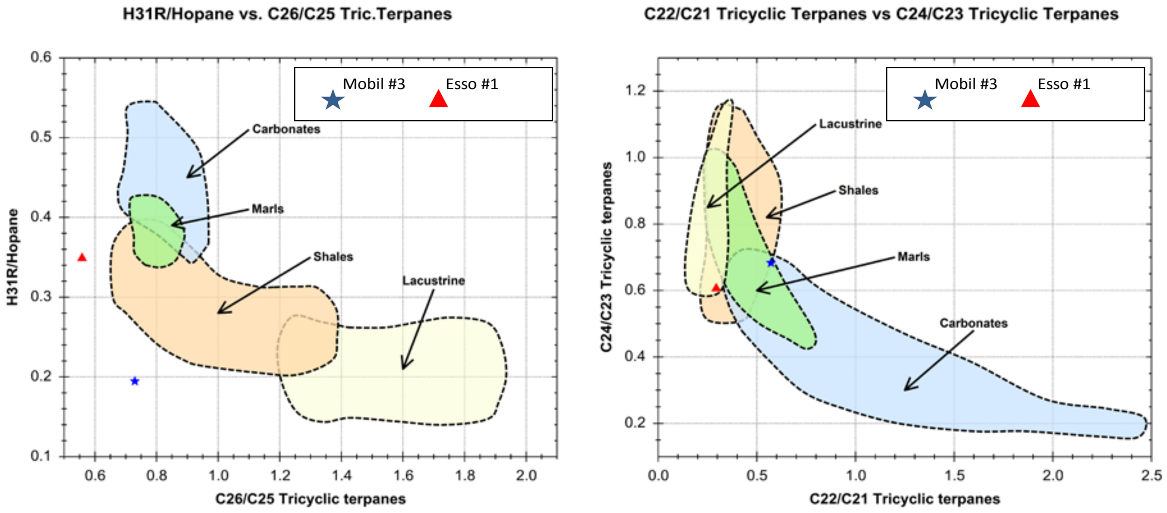

Figure 20.Cross plots of various tricyclic terpane and hopane ratios can be used to distinguish source rock lithology and depositional environment.

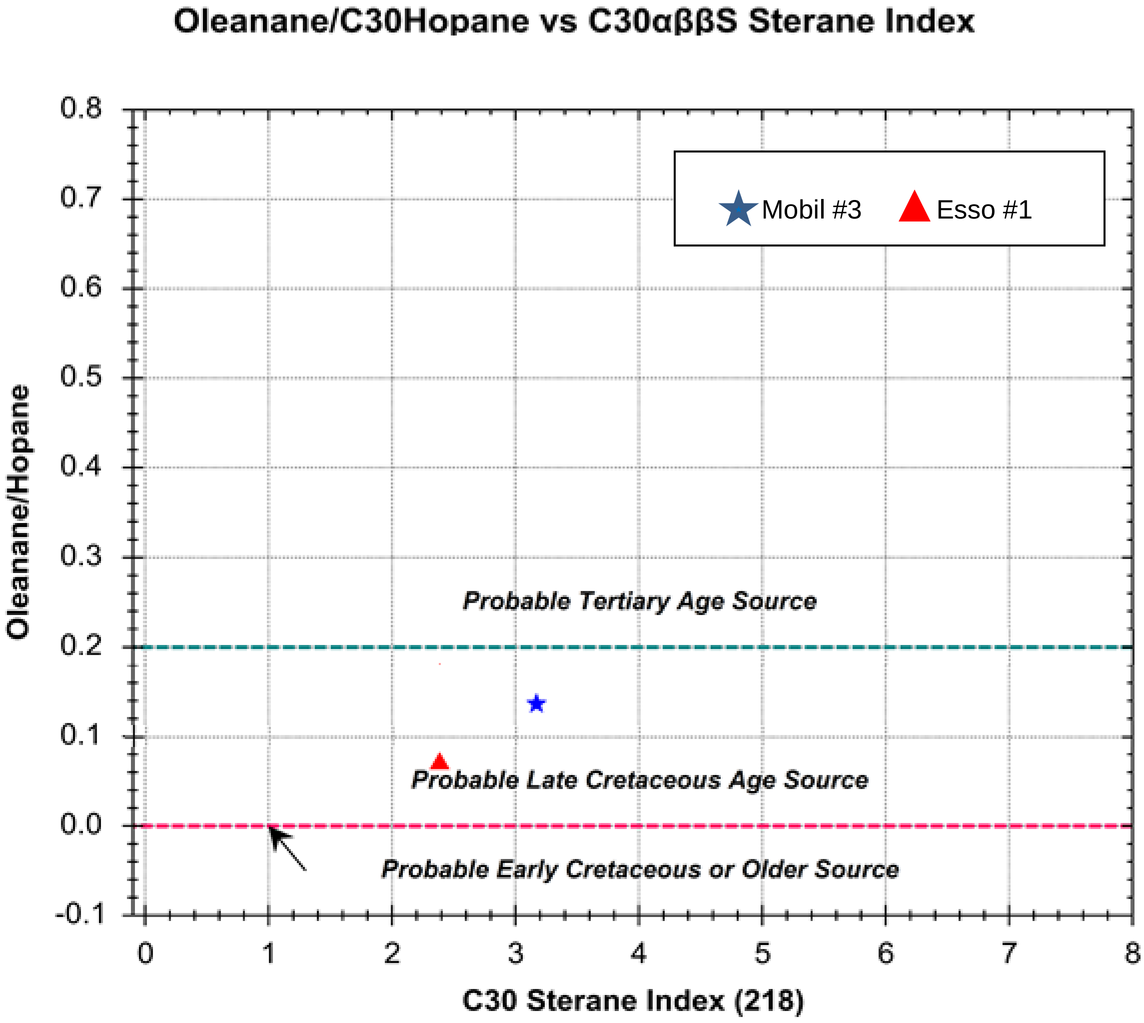

Figure 21.Cross plot of age-specific biomarkers. Note that the oleanane/hopane ratio includes both the 18β (H)-oleanane and 18α (H)-oleanane isomers.

Steranes within the Lower Cretaceous rock extract from the Esso #1 well are dominated by the diasteranes, but also contain variable to abundant regular steranes (Figure 18). Typically, abundant diasteranes implies that the samples have significant clay component to their mineralogy as opposed to dominantly carbonate and/or siliceous lithology. In the current investigation, this could suggest that overlying and adjacent Lower Cretaceous shale intervals are the more likely source rocks in comparison to the dominantly carbonate zone that was sampled for solvent extraction (7800-8130'). The regular sterane distributions in the Esso #1 extract (Figure 18) are dominated by C29 ααα components (~48%) with progressively lesser amounts of C27 and C28 (~30% & 22%, respectively). The relatively high abundances of the C29 steranes is fairly typical of source rocks with significant land-plant input, but is not always diagnostic and should be used in conjunction with other source related parameters (Peters et al., 2005).

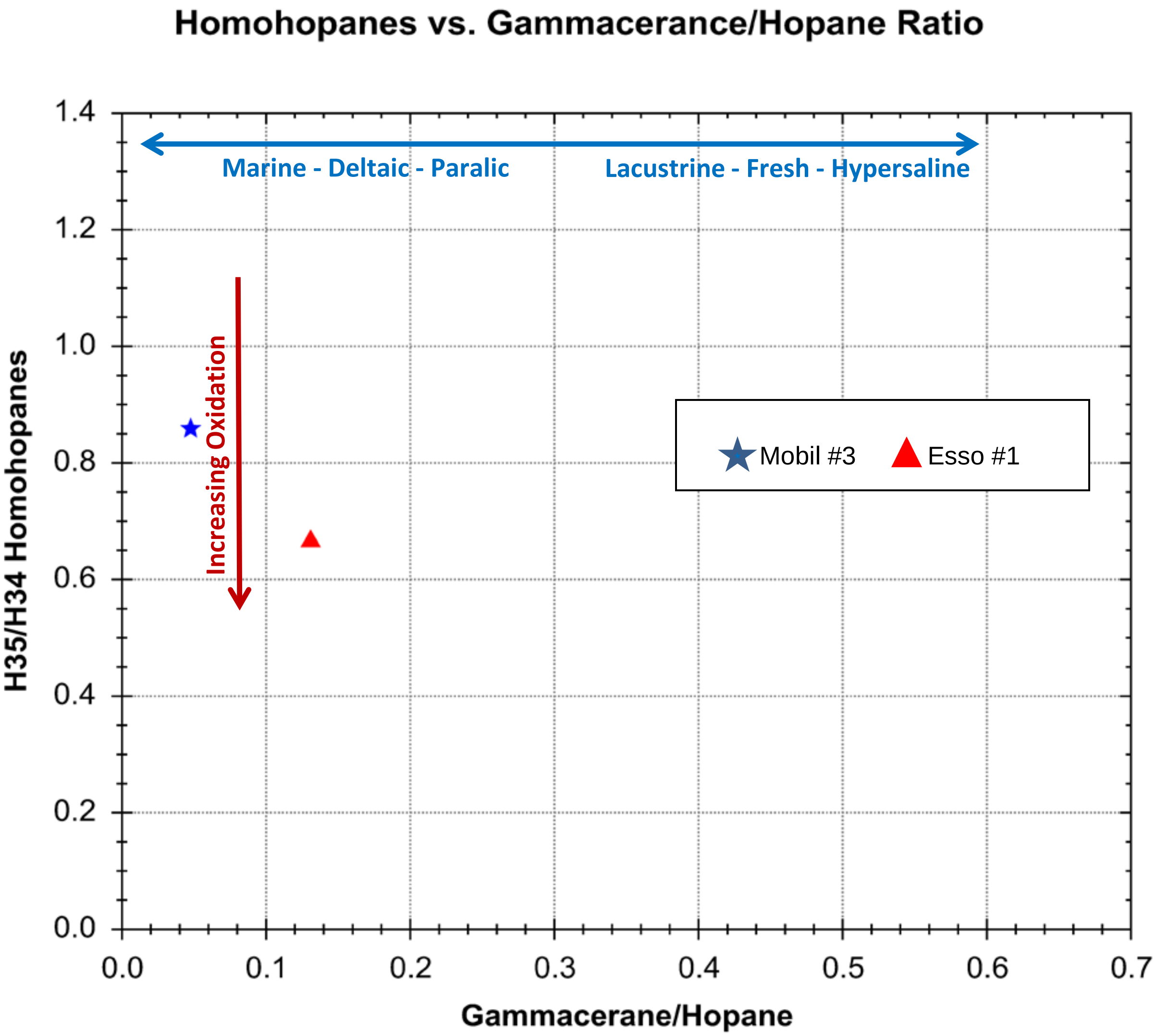

Figure 22.Plot of Gammacerane/C30 Hopane versus C35/C34 Homohopane ratio. The presence of high abundances of gammacerane indicates a stratified water column or hypersaline conditions. The C35/C34 homohopane ratio has been shown to differentiate oils from different depositional environments and is an indicator of redox conditions.

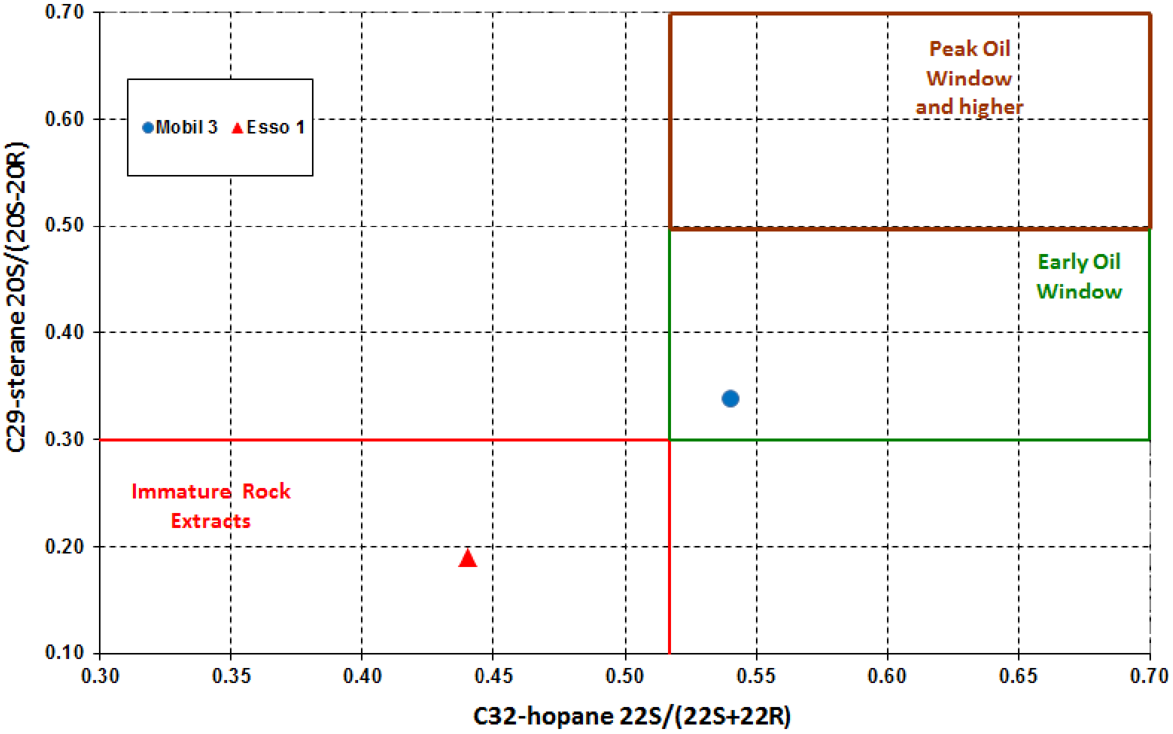

Figure 23. Biomarker maturity plot of hopane and sterane epimerization ratios.

Biomarker ratios have been evaluated in terms of thermal maturity in order to assist in determining if the extractable hydrocarbon signature from these Lower Cretaceous rocks matches the interpreted maturity based on other parameters (eg. Tmax and VRo). In general, the Esso #1 rock extract would appear to be immature with respect to the oil generation window on the basis of most biomarker ratios. The homohopane C32 S/(R+S) epimerization ratio of 0.44 appears to have not yet reached thermal equilibrium value of 0.6, which is thought to occur at an equivalent reflectance of 0.6% VRo (Figure 23). The moretane/hopane ratio of 0.34 also would appear to have not reached thermal equilibrium values of ~0.05, which occurs at an equivalent reflectance of 0.7% VRo. Likewise, the Ts/(Ts+Tm) ratio typically used for maturity assessment within the oil window is only 0.37 in this and has not reached thermal equilibrium values of 1.0, which typically happens at an equivalent reflectance of 1.4% VRo. The sterane C29 αααR S/(S+R) epimerization ratio of only 0.19 is well below thermal equilibrium values of 0.55 (Figure 23 & Figure 24) that are reached at an equivalent reflectance of 0.8% VRo. Similarly, the sterane C29 ββ/(ββ+αα) isomerization ratio of 0.11 that equilibrates at an equivalent reflectance of 0.9% VRo is also well below its endpoint value of 0.70 (Figure 24). These saturated biomarker data suggest a maturity level below 0.60% VRo and are consistent with other maturity parameters that indicate this Lower Cretaceous interval in the Esso #1 well is immature with regard to oil generation.

Maturity ratios based upon aromatic biomarkers can also offer another means of assessment that is particularly useful in sequences containing relatively high contributions of terrigenous organic matter. In the Esso #1 extract, the distributions of methylphenanthrenes (Figure 25) also support an interpreted thermal maturity that is immature with regard to oil generation.

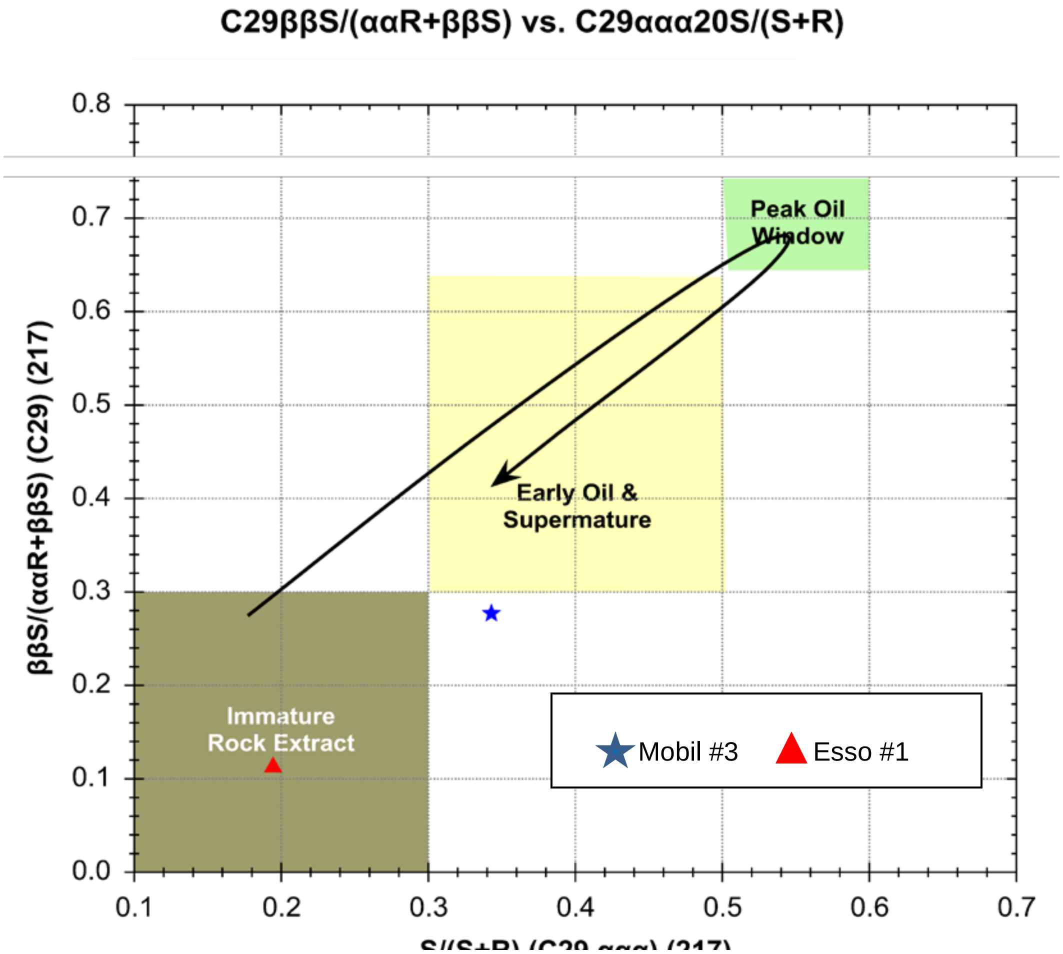

Figure 24. **Biomarker maturity plot of sterane isomerization and epimerization ratios.**

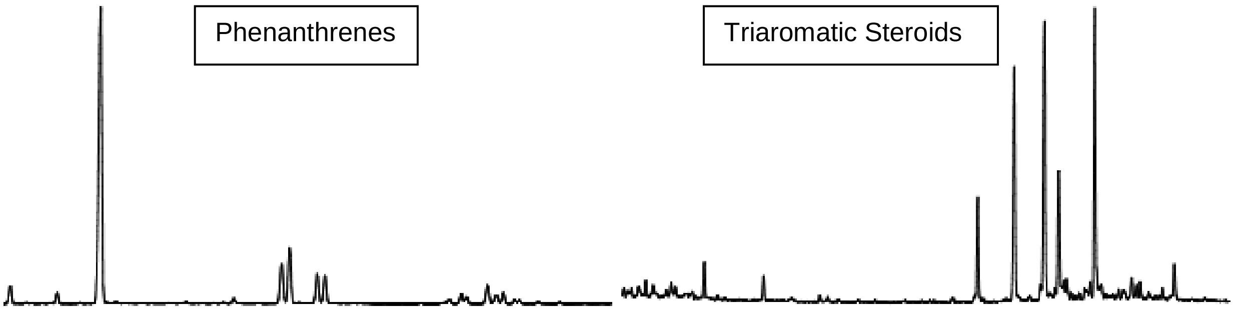

Figure 25. **Biomarker mass fragmentograms from the aromatic fraction of the Lower Cretaceous composite sample from the Esso #1 well (7800-8130'). The m/z 178+192+206 fragmentogram on the left illustrates the phenanthrenes, while the m/z 231 fragmentogram on the right illustrates the triaromatic steroids.**

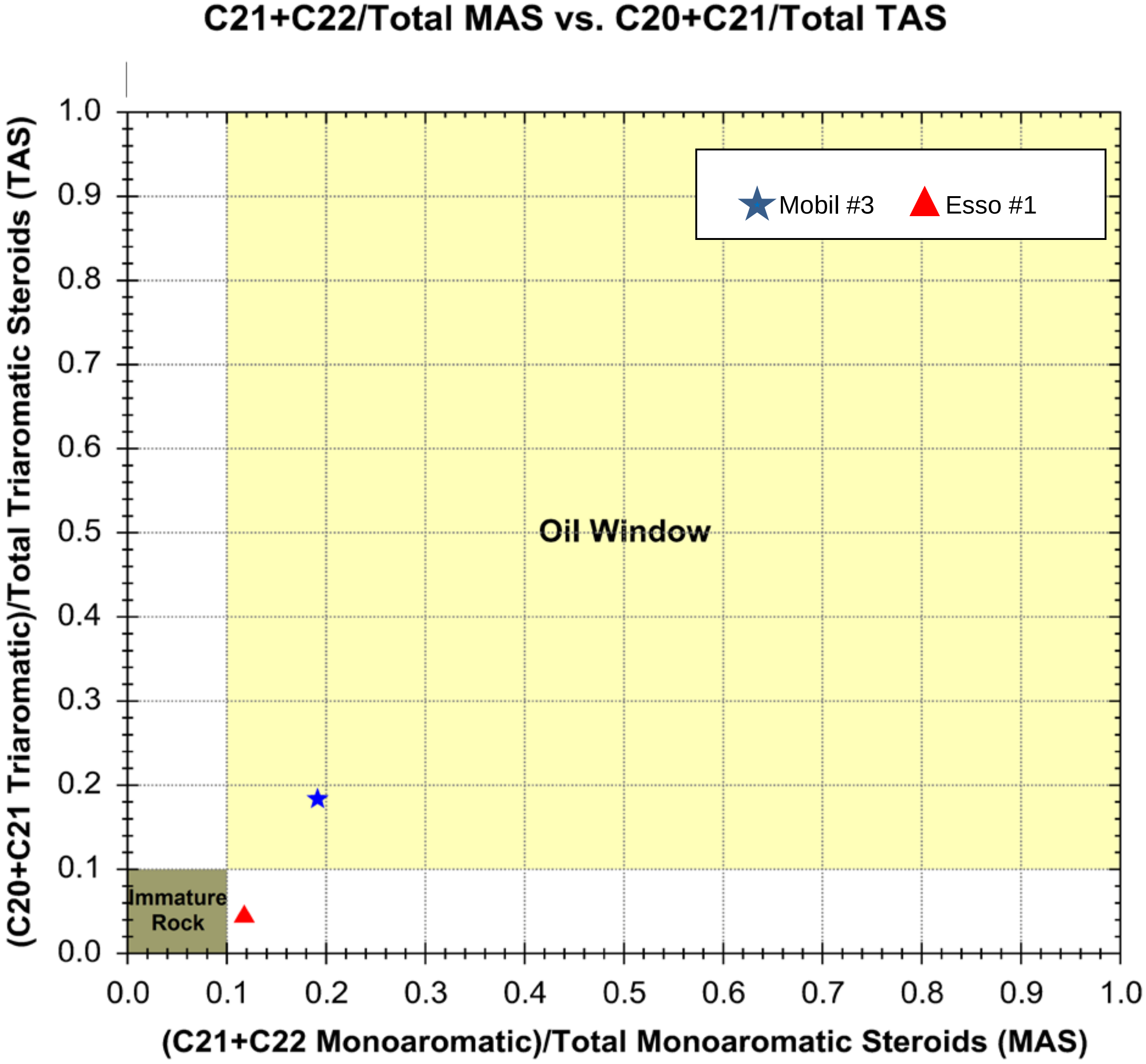

Figure 26.Biomarker maturity plot of monoaromatic and triaromatic steroid ratios for the Lower Cretaceous composite sample from the Esso #1 well (7800-8130').

MPI equivalent VRo value is 0.60% VRo, while those based on methlydibenzothiophenes indicate a much higher 1.58% VRo equivalency. These values should all be interpreted with some degree of caution since the calibration data sets used for these conversions typically involve coal sequences that are within the ~0.6 to 1.4% VRo range. Thus, the calibrations will not work for samples in which the thermal maturity is < 0.6% VRo. For this reason, useful maturity ratios could not be determined from other classes of aromatic compounds like the methylnaphthalenes and the dibenzothiophene based ratios are not considered valid.

The aromatic steroid distributions (Figure 25) in the Esso #1 extract also support an immature thermal maturity interpretation. The triaromatic steroid ratio of C28/(C28+C29) is 0.61, which is well below the thermal equilibrium value of 1.0 that occurs at an equivalent reflectance of 0.8% VRo. Likewise, the distribution of the short chain versus long chain mono- and tri-aromatic steroids (Figure 26) places the Esso #1 extract near the zone for immature rock extracts that are dominated more by the long chain components. The long chain aromatic steroids tend to be reduced at elevated maturity levels due to preferential thermal degradation and reach equilibrium at equivalent reflectance of around 1.0% VRo.

Mobil #3 Rock Extract

The bulk fractional composition of the Lower Cretaceous rock extract from the Mobil #3 well (Figure 27) is also composed of predominantly polar nitrogen, sulfur and oxygen (NSO) compounds (62%), with lower abundances of saturates (27%), aromatics (4%) and asphaltenes (7%). As noted previously, this is fairly common in recent sediments and immature samples that may contain a high abundance of organic acids, but it could also be an artifact of contamination. The GC fingerprint is also generally characterized by dominant contamination peaks likely associated with phthalate plasticizer components (Figure 27). However, the subordinate normal alkane envelope in this sample appears to have a more bimodal distribution with maxima in both the C17 and C24 range. The relatively high abundance of alkanes in the C21-C35 range is more typical of terrestrial higher plant input (Peters et al., 2005). Carbon Preference Index (CPI) value is 0.94, indicating an even carbon predominance that is more typical of marine carbonates and an extract that is thermally immature (Peters et al., 2005). The ratio of pristine/phytane (Pr/Ph) is near unity at 1.09, which offers minimal insights into paleoenvironmental redox conditions during deposition. This extract also has relatively low aromatic sulfur biomarkers as indicated by dibenzothiophene/phenanthrene (DBT/Phen) ratio of 0.04, which is more typical of marine shale lithologies. A cross-plot of the Pr/Ph ratio versus the DBT/Phen ratio place this Lower Cretaceous extract within the zone designated for marine and lacustrine shales (Figure 19).

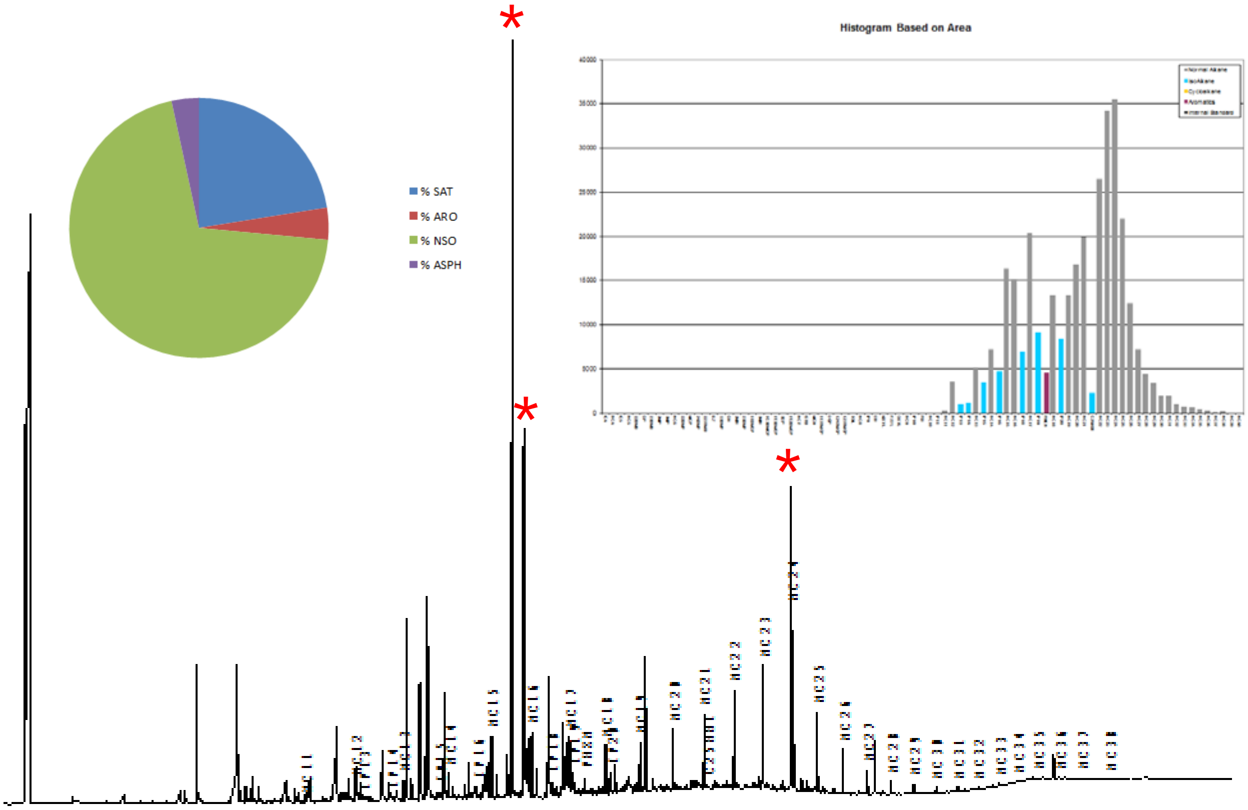

Figure 27.Solvent extract gas chromatogram of a Lower Cretaceous composite sample from the Mobil #3 well (5930-7309'). Insert pie diagram shows MPLC fractional composition of rock extract and histogram of alkanes (grey), isoprenoids (light blue) and aromatics (magenta). Peaks noted with red asterisk symbols are probable contaminants.

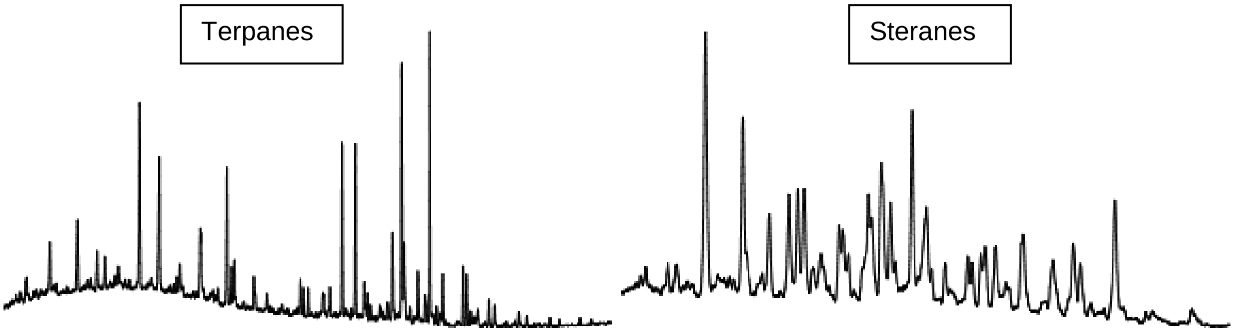

Figure 28. Biomarker mass fragmentograms from the aromatic fraction of the Lower Cretaceous composite sample from the Mobil #3 well (5930-7309'). The m/z 191 fragmentogram on the left illustrates the tri- and pentacyclic terpanes, while the m/z 217 fragmentogram on the right illustrates the diasteranes and steranes.

Biomarker data in the Mobil #3 extract show characteristic features which are similar for the most part to the previously discussed Lower Cretaceous extract from the Esso #1 well. There is a moderately high abundance of tricyclic terpanes (Figure 28) and the ratio of Tricyclic terpane/Hopanes is 0.87, which is somewhat lower than in the Esso #1 sample. The hopane distributions are dominated by C30 hopane, with lesser amounts of the C29 hopane, but there is a slightly higher relative abundance of the extended C31+ homohopanes (Figure 28). Using the relative distribution of various tricyclic terpane and hopane ratios to distinguish depositional environment and source rock lithology (Figure 20), the Mobil #3 sample plots away from the Esso #1 sample but it is still in in areas generally interpreted to be representative of marine shale source rocks.

The Mobil #3 extract has a fairly high oleanane/C30 hopane ratio of 0.14 and plots within the region of probable Late Cretaceous source rocks (Figure 21). Oleanane is considered a marker for both geologic age and source input, with higher abundances associated with greater higher plant input. This could be the reason why there is relatively more oleanane in the Mobil #3 extract in comparison to the Esso #1 well. The C30-sterane index in the cross-plot shown in Figure 21 generally increases with marine versus terrigenous organic-matter input into the source rock. For the Mobil #3 extract, the C30-sterane index value of 3.2 is fairly low, which would suggest significant terrigenous input. This biomarker data is in general agreement with organic petrology evidence showing a mixed kerogen maceral assemblage with on average 54% Type III kerogen composition in the Lower Cretaceous interval within the Mobil #3 well.

As noted previously, gammacerane is present in minor amounts in both samples analyzed in the current study. A cross plot of of Gammacerane/Hopane versus the C35/C34 Homohopane ratio (Figure 22) has been used to distinguish these Lower Cretaceous extracts in terms of their probable depositional environment. The relatively low Gammacerane/Hopane ratio of 0.05 in the Mobil #3 extract would imply fluctuating euxinic conditions within the marine depositional setting and this sample plots in the region of the diagram associated with marine-deltaic-paralic source rocks (Figure 22). The Mobil #3 extract has a C35/C34 homohopane ratio of 0.86 and plots in the region of more oxidizing depositional environment which is consistent with the generally low preservation of organic matter in these Lower Cretaceous rocks in this well.

Steranes within the Lower Cretaceous rock extract from the Mobil #3 well are also dominated by the diasteranes, but also contain variable to abundant regular steranes (Figure 28). Typically, abundant diasteranes implies that the samples have significant clay component to their mineralogy as opposed to dominantly carbonate and/or siliceous lithology. The regular sterane distributions in the Mobil #3 extract (Figure 28) are dominated by C27 ααα components (~39%) with progressively lesser amounts of C29 and C28 (~33% & 28%, respectively). The relatively high abundances of the C27 steranes is more typical of source rocks with significant marine organic matter input, but is not always diagnostic and should be used in conjunction with other source related parameters (Peters et al., 2005).

Biomarker maturity ratios for the Mobil #3 extract are consistently slightly higher in comparison to the Esso #1 sample, despite being from somewhat shallower depth. In general these ratios would suggest a maturity level in the Mobil #3 well that is still immature to marginally mature with respect to the oil generation window. However, the observed subtle differences in biomarker maturity ratios between the Mobil #3 and Esso #1 samples are somewhat unexpected. In the Mobil #3 well, the homohopane C32 S/(R+S) epimerization ratio of 0.54 is slightly below the thermal equilibrium values of 0.6, which is thought to occur at an equivalent reflectance of 0.6% VRo (Figure 23). The moretane/hopane ratio of 0.17 is lower than in the Esso #1 sample but still has clearly has not reached the thermal equilibrium endpoint of ~0.05, which occurs at an equivalent reflectance of 0.7% VRo. The Ts/(Ts+Tm) ratio of 0.5 is below thermal equilibrium values of 1.00 reached at an equivalent reflectance of 1.4% VRo. The sterane C29 αααR S/(S+R) epimerization ratio of 0.34 is below the thermal equilibrium value of 0.55 and the sterane C29 ββ/(ββ+αα) isomerization ratio of 0.28 is also well below its endpoint value of 0.7 (Figure 24). These saturated biomarker data suggest a maturity level below 0.60% VRo and are consistent with other maturity parameters that indicate this Lower Cretaceous interval in the Mobil #3 well is immature with regard to oil generation.

Maturity ratios based upon aromatic biomarkers have also been used to assess maturity in the Mobil #3 well as these ratios can be particularly useful in sequences containing relatively high contributions of terrigenous organic matter. In the Mobil #3 extract, the distributions of methylphenanthrenes (Figure 25) also support an interpreted thermal maturity that is immature with regard to oil generation. MPI equivalent VRo value is 0.60% VRo, while those based on methlydibenzothiophenes indicate a slightly higher 0.85% VRo equivalency. These values should all be interpreted with caution since the calibration data sets used for these conversions typically involve coal sequences that are within the ~0.6 to 1.4% VRo range. Thus, the calibrations will not work for samples in which the thermal maturity is < 0.6% VRo. For this reason, useful maturity ratios could not be determined from other classes of aromatic compounds like the methylnaphthalenes and the dibenzothiophene based ratios are not considered valid.

The aromatic steroid distributions (Figure 25) in the Mobil #3 extract also support an immature to marginally mature thermal maturity interpretation. The triaromatic steroid ratio of C28/(C28+C29) is 0.43, which is well below the thermal equilibrium value of 1.0 that occurs at an equivalent reflectance of 0.8% VRo. The distribution of the short chain versus long chain mono- and tri-aromatic steroids (Figure 26) is higher in the Mobil #3 extract and places it within the zone designated for the early oil window. This observation is consistent with other biomarker maturity data that suggest the Lower Cretaceous extract from the Mobil #3 well is slightly more mature in comparison to that from the Esso #1 well.

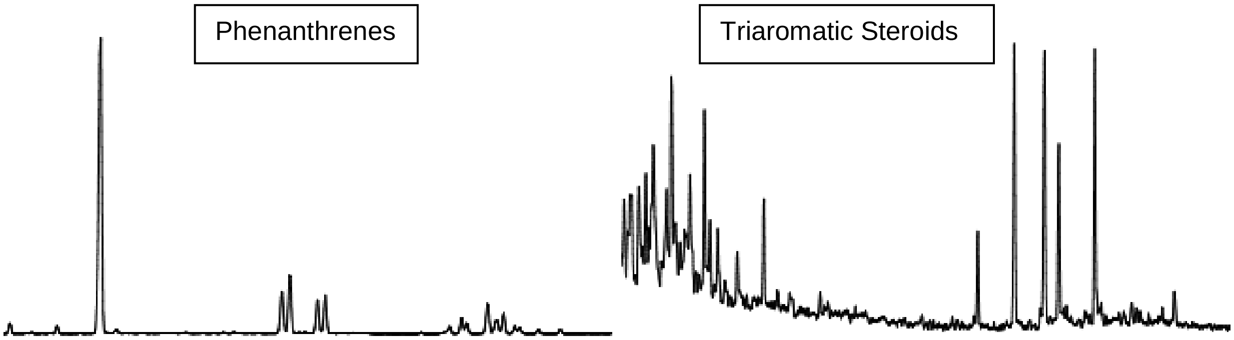

Figure 29.Biomarker mass fragmentograms from the aromatic fraction of the Lower Cretaceous composite sample from the Mobil #3 well (5930-7309’). The m/z 178+192+206 fragmentogram on the left illustrates the phenanthrenes, while the m/z 231 fragmentogram on the right illustrates the triaromatic steroids.

GEOCHEMISTRY SUMMARY

The Lower Cretaceous interval examined in the Esso #1 and Mobil #3 wells has generally poor source potential. Both wells clearly have some zones of elevated organic richness, but the average TOC values of 0.17 & 0.73 wt. % are considered poor to fair for consideration as a potential petroleum source rock. Organic matter is composed predominantly of gas-prone Type III kerogen along with variable amounts of oil-prone Type I & Type II kerogen and inert Type IV. Thermal maturity parameters from programmed pyrolysis, organic petrology and biomarker analysis suggest that the Lower Cretaceous interval in these wells is immature with regard to the oil generation window (~0.5% Ro). This amount of conversion would likely be sufficient to generate only trace amounts of hydrocarbons from this lean gas-prone/inert source facies.

There are two possible explanations that have been proposed for the occurrences of oil and gas shows within the Lower Cretaceous interval in these two wells. The first is that these represent residual hydrocarbons preserved in a regional carrier bed. In this scenario higher maturity expelled oil that originated from a source rock kitchen in deeper locations to the east migrated laterally and/or vertically into microscopic traps in porous Lower Cretaceous strata on the North Carolina continental shelf. The second possible explanation for the occurrence of these deeper oil and gas shows is that the hydrocarbons could be locally sourced (in-situ) by very early bitumen generation from Lower Cretaceous source rocks at low maturity with limited migration.

The geochemical evidence collected in the current study offers some additional insights into which of the previously proposed hypotheses are more likely. However, the interpretation of the new geochemical data is not unequivocal and does not conclusively resolve the issue. Maximum TOC of prospective cuttings samples from these two wells is 1.05 & 9.30 wt. %, which would suggest that some Lower Cretaceous zones would have the potential to generate and expel hydrocarbons at elevated thermal maturity. However, thermal maturity estimations from a variety of geochemical methods show that the Lower Cretaceous intervals in both of these wells are immature with regard to the main oil generation window (~0.5% VRo). Thus, if the hydrocarbons detected in these wells are autochthonous then they are more likely to represent low thermal maturity bitumen generation with limited migration. Evidence supporting this explanation comes from the petrographic observations of the occurrences of solid bitumens within several of these samples (Figure 6 through Figure 10). Most of these bitumen occurrences are discontinuous and thus do not appear to represent an interconnected oil migration pathway. Also, bulk fractional composition of Lower Cretaceous rock extracts from these wells are composed of predominantly polar nitrogen, sulfur and oxygen (NSO) compounds (62%), with lower abundances of saturates (27%), aromatics (4%) and asphaltenes (7%). This is more typical of low thermal maturity bitumens as opposed to high maturity oils. In-situ hydrocarbon saturations as measured by programmed pyrolysis are very low and average only 0.10 mg HC/g rock or 2 bbl/a-ft in both wells. Likewise, PI and NOC values in these rocks are also low to moderate. This suggests a very low amount of in-situ hydrocarbon saturation. Given the generally low hydrocarbon saturations and the sporadic and variable NOC and PI values, it would seem more likely that these are associated with sporadic locally generated in-situ bitumen occurrences rather than a wide spread regional migration pathway. However, the conditions of storage and age of these samples prior to geochemical analysis could render such interpretations invalid. Any high maturity volatile in-situ oil saturation would surely have been lost in the +50 years prior to analysis no matter the storage conditions. Also, volatile loss could account for the relatively high fractional abundance of NSO compounds in the composite rock extracts from these wells.

From an organic petrology standpoint, the occurrence of solid bitumens within several of these samples could be viewed as evidence of in-situ generation (as noted previously). However, details of these petrographic observations may suggest otherwise. In this alternate interpretation of the data it would appear unlikely that the observed bitumen was generated in-situ because:

a) The amounts of kerogen observed as a percentage of the whole rock are so small, <1% in most cases, and diffuse.

b) The only macerals that occasionally occurred in amounts >1% are vitrinite and inertinite and these are not particularly conducive to oil generation.

c) The bitumen observations occurred within the mineral matrix of the rock samples and did not appear to occur within or adjacent to kerogenous source rock material.

The photomicrographs from these Lower Cretaceous samples only show choice examples of the small amounts of fluorescing liptinite or liptinite-rich vitrinite and are certainly not representative of the samples as a whole. Thus, the impression that there are significant and/or concentrated occurrences of oil-prone organic matter in these samples may not be valid. Continuous bitumen networks are easier to observe in intact core samples but unfortunately all observations in the current study were performed on crushed material. Thus, the organic petrologist may not have seen continuous ‘migrabitumen’ lenses but there were hints of them (Figure 8). Samples where bitumen occurs could be near the outermost point laterally from the pathway proper, whereas the mysterious bluish-white fluorescing mineral fractures observed in the shallowest Neogene aged sample (810’) may be evidence of preserved preferentially leaked/vertically migrated light hydrocarbons (although analogous fluid inclusion studies suggest caution when interpreting fluorescence colors, eg. George et al., 2001). In the Esso #1 well, the majority of hydrocarbon observations in the Lower Cretaceous occurred over a specific sample interval (7705’-7949’) and this observation is more consistent with an artefact from a migration pathway rather than the development of more widespread in-situ bitumen generation. This interval may require a more detailed examination in future studies that could include potential examination of the molecular composition of oils trapped within fluid inclusions associated with this potential migration pathway. Such techniques have been previously proven useful in oil fields like the Gippsland Basin in Australia (George et al., 1998), which also has documented occurrences of migration contamination (Philp and Gilbert, 1982, 1986; Murray et al., 1998).

Biomarker data collected from the composite extracts in the Esso #1 and Mobil #3 wells also offers insights into source input, lithology, thermal maturity and geologic age. The general conclusions from analysis of the saturate and aromatic fraction biomarkers in these two Lower Cretaceous extracts are as follows:

a) The samples appear to contain input from both terrigenous and marine organic matter input (eg. alkane, sterane distributions) deposited in a fairly oxic depositional environment.

b) The samples appear to originate from source rocks that were dominantly marine shale lithology (eg. high diasteranes, low DBT/P, tricyclic terpane distributions).

c) The samples are likely to be Cretaceous age (eg. oleanane).

d) The samples are low thermal maturity, with the Esso #1 well having immature biomarker ratios and the Mobil #3 well having ratios in the immature/early mature range.

All of these observations are consistent with an in-situ origin for the biomarkers contained in the composite rock extracts. In particular, the presence of the age-specific biomarker oleanane strongly correlates the extractable hydrocarbons with a Lower Cretaceous source. This would appear to eliminate a down dip Jurassic aged source rock as a candidate for an oil charge that might be represented as shows along a migration pathway in these wells. Thermal maturity considerations would appear to strongly support an autochthonous origin for the extractable hydrocarbons since the maturity levels are in agreement with rock derived maturity parameters like T_{max} and VRo that all indicate a low thermal maturity which appears to be immature with respect to the main oil generation window.

While this biomarker data would appear to conclusively establish an in-situ origin for the hydrocarbons present in the Lower Cretaceous intervals in these two wells, the possibility of migration-contamination must be considered. This process occurs when a migrating or trapped crude oil functions as a solvent, dissolving molecular components from the syndepositional organic matter of the migration conduit and/or reservoir rock (see Curiale, 2002 for review article). If such a process were occurring in the wells examined in the current study, then the biomarker data would not be unequivocal evidence for an autochthonous origin since it could have originated by solubilisation of indigenous organic material by a migrating oil charge.

In the present study, no such maturity imbalances were noted between compound classes like the methylphenanthrenes and ethylcholestanes. All saturate and aromatic biomarker maturity ratios were in general agreement and suggest low thermal maturity levels. Thus, there appears to be no molecular geochemical evidence to support a migration conduit hypothesis for the origin of the hydrocarbon staining and shows present within the Lower Cretaceous interval in the Esso #1 and Mobil #3 wells. However, even this data is not unequivocal in terms of interpretation. It remains possible that the remnant migrating oil fingerprint is simply overwhelmed by extractable bitumen from the indigenous organic matter in these rocks to such an extent that even molecular ratios like the aromatic methylphenanthrenes are compromised. This is certainly plausible and given the relatively high abundance of terrigenous organic matter in these samples (which contains relatively abundant extractable aromatic compounds).

One other consideration should be taken into account with regard to the use of the oleanane biomarker to age-date the samples in the current investigation. Coffey and Sunde (2009) present limited geochemical data from a single source rock extract sample in the Esso #1 well (8505'). In this sample they also noted the occurrence of oleanane and give a reported oleanane/C30 hopane ratio of 0.05, which is just slightly lower than the 0.07 value reported in the current investigation for the Lower Cretaceous composite sample from the Esso #1 well (7800-8130'). Most of the other biomarker ratios in this particular sample, which has been inaccurately dated as Upper Jurassic (J. Coleman, per. comm., 2017), are also very similar to those reported in the current study. This sample does have somewhat lower relative abundances of tricyclic terpanes and thermal maturity ratios, such as Ts/Tm, are somewhat higher compared to the samples analysed in the current study. The low abundances of oleanane in the range reported for these samples (~0.10) have also been documented to occur in Jurassic crude oils (Peters et al., 1999) and rock extracts (Moldowan et al., 1994) and extracts of megafossils from Permian rocks (Taylor et al., 2004). Thus, the presence of the oleanane biomarker in relatively low concentrations within the rock extracts examine in the current study may not be entirely definitive with regard to age-dating and origin.

In conclusion, the irrefutable source of the hydrocarbons present in the Lower Cretaceous intervals within the Esso #1 and Mobil #3 wells is inconclusive due to conflicting suggestions from different data sources. However, based on the extremely low concentrations and sporadic nature of hydrocarbons in the samples which have been examined, there is no evidence for either substantial in-situ generation or the presence of a significant migration pathway.

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Appendix 2 - Pyrolysis reports (total organic carbon [TOC] and Rock-Eval 6 [RE6])

Esso Hatteras Light #1 well – TOC data

Esso Hatteras Light #1 well – RE6 pyrograms

Esso Hatteras Light #1 well – representative vitrinite trend and reworked vitrinite populations

Mobil State of North Carolina #3 well – TOC data

Mobil State of North Carolina #3 well – RE6 pyrograms

Appendix 3 - Vitrinite reflectance (photomicrographs, %R_o, whole rock percentages

Esso Hatteras Light #1 well – photomicrographs

Esso Hatteras Light #1 well – %R_o measurements

Esso Hatteras Light #1 well – %R_o whole rock percentages