

## PROVENANCE AND MIGRATION OF THE PETROLEUM FLUIDS IN THE WESSEX BASIN, SOUTHERN ENGLAND

### GÜNEY İNGİLTERE'DEKİ WESSEX HAVZASINDA PETROLÜN KÖKENİ VE GÖÇ YOLLARI

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#### ABSTRACT

Despite being one of the most important petroleum basins in Western Europe, the Wessex Basin has not yet been fully studied in terms of migration of the petroleum fluids, the maturation of the hydrocarbons and the detailed correlation between the oil seepages and the potential source rocks. The aim of this study is to correlate oil seepages to the source rock(s) by biomarker analysis and to establish the kitchen areas in the basin by using 1D basin modelling and finally to integrate the results in order to understand the hydrocarbon provenance and possible migration pathways in the Wessex Basin.

There are several possible Mesozoic source intervals in the basin: the Lower Lias Black shales –or “Blue Lias”-, the Oxford Clay, the Kimmeridge Clay, the Purbeck Shales and Limestones, the Nothe Clay and the Gault Clay. Firstly, basing modelling studies had been conducted in order to identify mature source rocks among them. Basin modelling suggests that among these source rocks, only the Lower Lias and, partially, the Oxford Clay is mature in some wells. These two source rocks were buried deeply enough to the south of the Purbeck-Isle of Wight Disturbance. To the north of the disturbance all the source rocks were proven to be immature in all wells. Petroleum charging requires a North along with NW and NE migration from source kitchen to the existing traps with both lateral and vertical migration route. Besides, TR vs Time plot indicates that hydrocarbon generation started in the Early Cretaceous; peaked in the Middle-Late Cretaceous and ceased before Tertiary uplift since it caused source rocks to cool down and to stop hydrocarbon generation.

Finally, biomarkers had been analysed for the oil seepages and the mature source rocks which were

identified from the basin modelling. Biomarker analysis suggests that all the seep samples might have similar depositional origin with similar thermal maturity. The rock samples, however, have immature signatures from the  $Ts/Ts+Tm$  and  $20S/(20S+20R)$  C29 sterane maturity parameters. The Blue Lias and the Oxford Clay samples show immaturity because the samples were collected to the north of the Purbeck-Isle of Wight Disturbance, where all the source rocks are immature. It may be suggested that the oil seepages are likely to correlate with either BL or OC or both based on biomarker abundance and hopane and sterane distribution. However, based solely on organic geochemistry and biomarker analysis the BL and OC samples were not be able to be distinguished as they both contain type II kerogen and both have very similar biomarker distribution and organic chemistry properties.

#### ÖZ

Batı Avrupa'da petrolcülük açısından en önemli havzalarından biri olan Wessex Havzası, hidrokarbon olgunlaşması, olası göç yolları, petrol-kaynak kaya korelasyonu açısından şimdiye dek tam manasıyla çalışılmamıştır. Bu çalışmanın amacı, biomarker analizleri yardımıyla petrol sızıntısı-kaynak kaya korelasyonu yapmak ve 1D havza modellemesi ile petrol oluşum alanlarını belirleyerek Wessex Havzası'ndaki petrolün kaynağına ve olası göç yollarına bir yaklaşımda bulunabilmektir.

Havzada Mesozoyik yaşlı bir çok potansiyel kaynak kaya mevcuttur. Bunlar: Alt Liyas Siyah şeylleri –diğer adıyla Mavi Liyas-, Oxford Şeyli, Kimmeridge Şeyli, Purbeck Şeyli ve Kireçtaşları, Nothe Şeyli ve Gault Şeylleri'dir. Havzadaki bu kaynak kayalardan hangilerinin yeterli olgunluğa ulaştığını belirlemek amacıyla ilk olarak havza modellemesi yapılmıştır.

Havza modellemesine göre bu potansiyel kaynak kayalardan yalnızca Alt Liyas ve kısmen de Oxford Şeyli olgundur. Bu iki kaynak kaya Purbeck- Purbeck-Isle of Wight Fay Kuşağı'nın güneyindeki alçalmış bloğunda yeterli olgunluğa erişebilecek kadar gömülmüştür. Bu kuşağın kuzeyindeki bütün kuyularda potansiyel kaynak kayaların hiçbiri olgunlaşmamıştır. Bu durumda, güneyde yer alan petrol oluşum alanında türeyen petrolün daha kuzeydeki kapanları doldurabilmesi için kuzeye doğru yatay ve düşey göç yolları gerekmektedir. Ayrıca, TR vs. Time grafikleri de petrol türümünün Erken Kretase'de başladığını, Orta-Geç Kretase'de zirveye ulaştığını ve Tersiyer'de meydana gelen yükselme nedeniyle bu kaynak kayaların soğuyup türümlerini durduduğunu göstermektedir.

Daha sonra, havza modellemesine göre olgun olan bu kaynak kayalar ve petrol sızıntıları üzerinde biomarker analiz çalışmaları yapılmıştır. Biomarker analizlerine göre bütün petrol sızıntısı örnekleri benzer olgunluklara ve benzer depolanma koşullarına sahiptirler. Fakat numune örneklerine ait Ts/Ts+Tm ve 20S/(20S+20R) C29 sterane olgunluk parametreleri olgunlaşmamaya işaret etmektedir. Mavi Liyas'a ve Oxford Şeyllerine ait örnekler olgunlaşmamış (immature) çünkü bu numuneler bütün potansiyel kaynak kayaların olgunlaşmamış olduğu, Purbeck- Purbeck-Isle of Wight Fay Kuşağı'nın kuzey tarafından alınmıştır. Biomarker miktarına ve hopane-sterane dağılımlarına göre incelenen petrol sızıntı örnekleri Mavi Liyas ve/veya Oxford Şeyllerinden türemiş olabilir. Fakat Mavi Liyas ve Oxford Şeyllerinin her ikisi de tip II kerojen içerdiğinden ve biyomarker dağılımları ile organik kimya özelliklerinin çok benzer olmalarından dolayı yalnızca organik kimya ve biomarker analiz yardımıyla bu iki kaynak kaya birbirinden ayıramamaktadır.

Key Words: Wessex, biomarker, basin modeling, Blue Lias

## INTRODUCTION

The Wessex Basin occupies an area of 80,000 km<sup>2</sup> (Kent 1949) and it is one of the most important petroleum basins in the UK (Figure 1). Hydrocarbon exploration within the basin started in 1934 based on existing anticline structures and numerous oil seeps within the basin. The first well was drilled in the Wessex Basin in 1937 by the D'Arcy Company. The first field that was discovered within the basin is the Kimmeridge Field in 1959, from which 370 bbls/day of oil are being produced for 30 years. Although this was a small discovery, it led to the discovery of

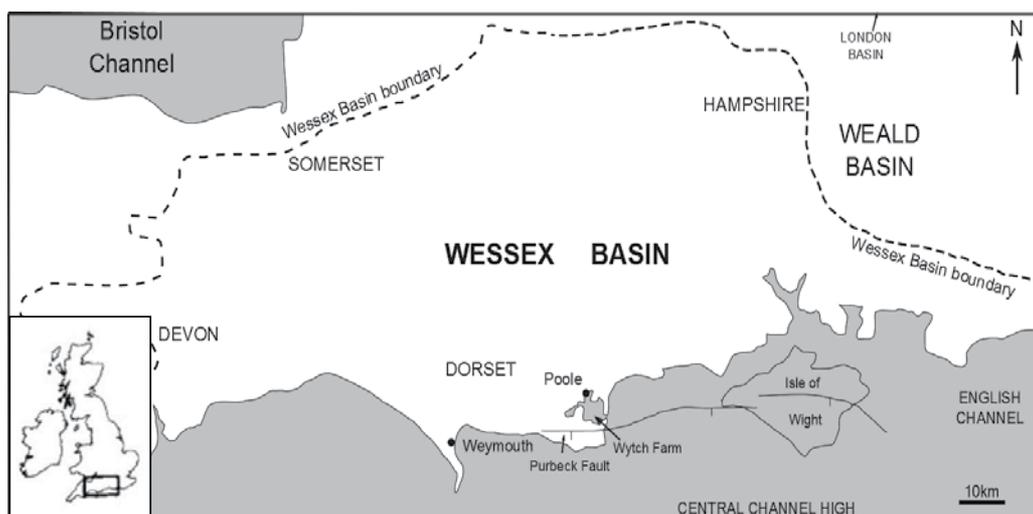
Northwest Europe's biggest onshore oilfield, Wytch Farm with about 500 MMBbls of hydrocarbon reserves. Other oilfields in the basin are Wareham, Stoborough and Durlston Head.

There are several oil seeps that occur along the Dorset coast. Selley (1992) mentioned 13 locations of seepage in the Wessex Basin (Figure 2). Upwey (Purbeck Formation), Osmington Mills (Benclyff Grit Fm), Holworth House (Purbeck Fm), Chaldon (Purbeck Fm), Durdle Door (Purbeck and Wealden formations), Dungle Head (Wealden Fm), Lulworth Cove (Wealden Fm), Mupe Bay (Purbeck and Wealden formations), Worbarrow Bay (Wealden Fm), Kimmeridge Bay (Kimmeridge Clay Fm), Kimmeridge (Portland Fm), Anvil Point (Purbeck Fm) and Pevril Point (Purbeck Fm). In addition to this list, Lulworth Banks (oil & gas from Corallian Fm), Duckworth, St Oswalds Bay (Wealden Fm; Selley and Stoneley, 1984), Portland (Portlandian; Lees and Cox, 1937) and Stair Hole, Lulworth (Wealden Fm; Bigge and Farrimond, 1998 and Purbeck; Lees and Cox, 1937) are also observed seepages in the basin. There is also a small gas discovery by the well 98/11-2 and a non-commercial gas discovery at South Barn in the vicinity of Swanage.

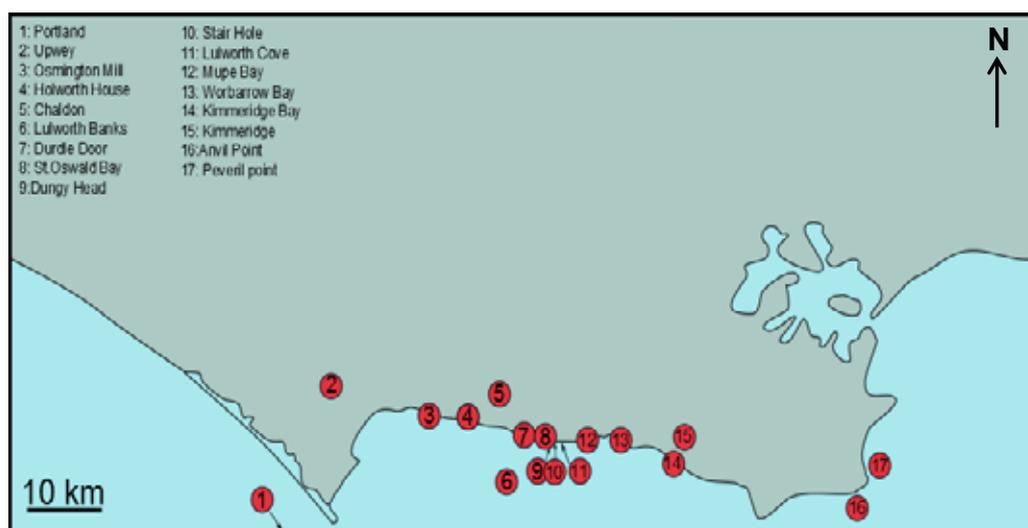
There are three main organic-rich Mesozoic source rocks within the Wessex Basin, which have been studied for a long time, (a) the Lower Lias shales (Blue Lias), (b) the Oxford Clay and (c) the Kimmeridge Clay Formation. There are also other organic-rich source rocks in the study area such as the Gault Clay, the Purbeck Black Shale and the North Clay. However, these Mesozoic intervals have attracted little or no attention by the researchers. In this study, these units are also examined for better understanding of the hydrocarbon provenance within the Wessex Basin.

## Location

The Wessex Basin is located in southern England (Figure 1) and comprises a series of post-Variscan sedimentary sub-basins and intra-basinal highs that formed across southern England and adjacent offshore areas (Underhill and Stoneley, 1998). Ziegler (1990) suggested that the Wessex Basin contains a number of extensional sub-basins which formed part of Mesozoic intracratonic basins. The Wessex Basin extends through Hampshire and Dorset and through some parts of East Devon, Somerset and Wiltshire. Armorican and Cornubian Massifs are located to the west and southwest; London Platform (aka London-Brabant Massif) to the north and the



**Figure 1.** Location of the study area. Dash line shows the estimate boundary of the Wessex Basin.



**Figure 2.** Oil and gas seepage locations in the Wessex Basin. Based on Selley (1992) (Locations 1, 6, 8 and 10 are gas seepages and the rest are oil seepages in the basin)

Central Channel High to the south (Figure 1). However, north-eastern and north-western boundaries have not been defined yet (Underhill and Stoneley, 1998). The Hampshire-Dieppe High separates The Wessex and Weald Basins. While the boundary between them is not clear, they might have formed a single depositional basin in Mesozoic times (Scott & Colter, 1987).

### Basin Structure

The Wessex Basin contains four half-graben sub-basins: The Pewsey Sub-basin, the Mere, or Vale of Wardour Sub-basin, The Dorset Sub-basin (Winterbourne Kingston Trough) and the Channel, or Portland-Wight Basin. All these sub-basins were

formed and modified by south-dipping listric normal faults (Chadwick 1993). These Mesozoic basins began to form by the Permian rifting episode which is related to early attempt of opening of the North Atlantic Ocean. The rifting peaked in Jurassic and continued up to the Middle Cretaceous (Arkell, 1947; Zigler, 1975; Kent, 1997; Stoneley 1982). A regional subsidence occurred during the rifting phase. These events caused faulting along weak structural lines such as the South Dorset-Isle of Wight Fault as known as Purbeck-Isle of Wight Disturbance (Arkell 1947; Colter and Harvard, 1981)(Figure 3). Three other tectonic movements occurred during the Cretaceous: (1) the pre-Albian movement which formed faults and folds and resulted in erosion of the Juras-

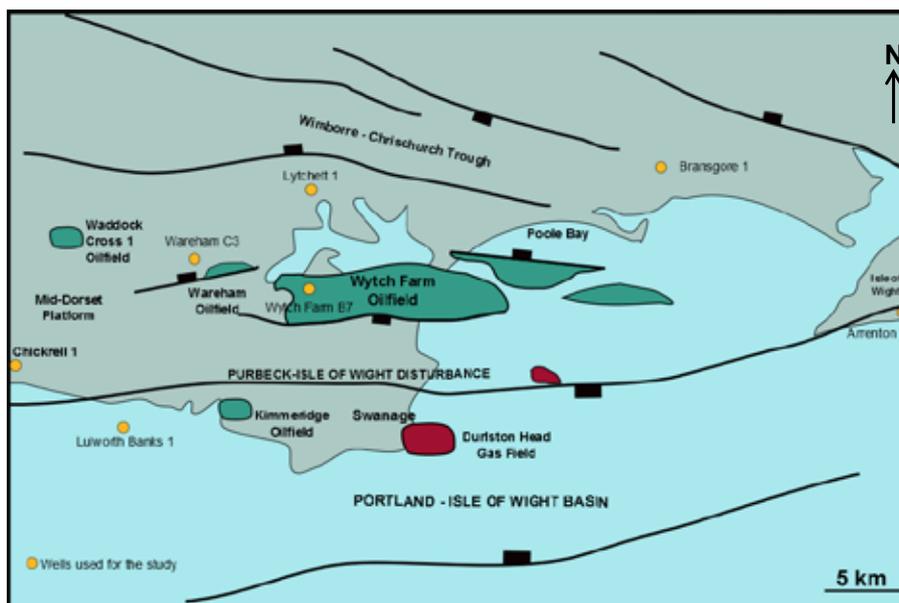


Figure 3. Oil and gas fields and major structural elements of the Wessex Basin.

sic and Lower Cretaceous strata. (2) a Lower Albian movement, which caused tilting and subsidence of the region. (3) an Upper Cretaceous and the Lower Tertiary movement which led to the regression of the Chalk Sea, tilting and folding the strata within the region (Ebukanson & Kinghorn 1986a). The extensional movement within the region is believed to have ceased in the Aptian. This is followed by a Tertiary tectonic inversion which is related to the Alpine Orogeny, which caused folding, thrusting and reactivation of pre-existing extensional faults within the area (Colter and Harvard 1981). The growth or syn-depositional faults controlled depositional strata thicknesses throughout the Triassic, Jurassic and Early Cretaceous. After the Early Cretaceous, the stress regime changed to compressional, resulting in the reverse movement of the existing faults and the formation of inversion structures within the basin. It is estimated from the well data 98/11-2 and 98/23-1 that the amount of uplift is 500 m to the north of the Purbeck-Isle of Wight Fault and 1-2 km to the south of the fault and to the north of the Central English Channel Fault (Law 1998).

### Aims and Objectives of the Study

Although Wessex Basin is one of the most hydrocarbon-prospective UK basins, it has not yet been fully studied in terms of migration of the petroleum fluids, the maturation of the hydrocarbons and the detailed correlation between the oil seepages and the potential source rocks. Until now, there is no general agreement on the migration pathway from

the kitchen areas to the reservoir rocks and which source rock(s) provide oil and gas accumulations in the Wessex Basin (Cornford et al., 1988).

Therefore this study aims at:

(i) typing/correlation of the hydrocarbon occurrences in the Wessex Basin to the possible petroleum source rocks by using biomarker analysis in order to establish the petroleum provenance in the basin;

(ii) establishing the kitchen areas in the basin by using 1D basin modelling;

(iii) establishing the migration pathways from the kitchen areas to the reservoir rocks.

The key methodology of the study is:

(i) Field work to sample oil seeps and petroleum source rocks in the Wessex Basin;

(ii) Analysis of the oil and shale samples to identify common provenance;

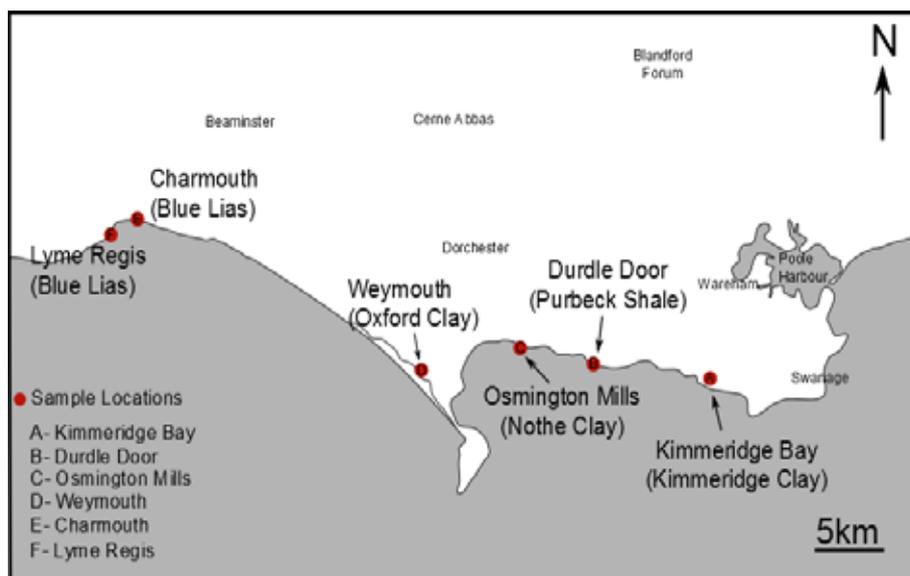
(iii) 1D basin modelling to identify possible "kitchen" areas;

(iv) Sedimentological study to identify possible rocks, where fluids can migrate;

(v) Study of the various faults that can provide pathways to migration of petroleum fluids.

### Dataset and Workflow

A variety of data were used for this study: 7 rock samples and 6 oil-stained samples (oil seeps) were collected from various outcrops for the geochemical analyses (Table 1). Well data for basin modelling are from published sources, the British Geological Survey (BGS) and the UK Onshore Geophysical Li-



**Figure 4.** Map showing the sample locations (Note that Gault Clay is not showing on the map since the sample for this SR was obtained from other research study.).



**Figure 5.** Photos of the rock samples are the Blue Lias (BL1 and BL2), the Kimmeridge Clay (KC), the Oxford Clay (OC), the Purbeck Shale (DD), the Gault Clay (GC), the Nothe Clay (NC). Photos of the oil-stain samples are Osmington Mill (OM), Mupe Bay (MB), Stair Hole (ST).

brary and previous literature and geological maps were used for better regional understanding and integration of geochemical analyses result with the basin modelling.

## SAMPLES AND METHODS

### Outcrops and Sample Descriptions

Samples were collected at various locations (Figures 4). Table 1 shows the locations of the samples as well as the ages of the rock samples. There are seven rock samples and six oil-stained samples used in this study. The Blue Lias (BL-1 and BL-2) samples are dark grey and finely laminated shales. The Kimmeridge Clay (KC) sample is grey, hardened mudstone and shows no lamination as the BL samples. The Oxford Clay (OC) is dark brown and dark grey colour laminated shale. The Purbeck Shale (DD) sample shows fissile texture and has grey-dark grey colour. The Gault Clay (GC) is grey silty mudstone with some coarser grains and shows no lamination. DD and GC samples were obtained from different researcher in the Wessex area. The Nothe Clay (NC) is darker grey compared to GC sample. The ST sample is oil-stain clastic deposits of the Wealden Group. OM is dark brown oil stain sample from Osmington Mill. The MB sample is the most distinctive one among the oil-stain samples because it is dark, black colour and heavily stained heavy-oil smelling sample. The D2, D3 and D4 samples are from the Purbeck Group. They are oil-stained rock samples taken from Durdle Door. The D2 and D3 are oil-stained limestones and the D4 is

Rock Sample	Location	Age	Seep Oil	Location
Blue Lias (BL1)	Lyme Regis	Kimmeridgian	Osmington Mill(OM)	Osmington Mill
Blue Lias (BL2)	Charmouth	Toarcian	Mupe Bay(MB)	Mupe Bay
Kimmeridge Clay (KC)	Kimmeridge Bay	Toarcian	Stair Hole (ST)	Stair Hole
Oxford Clay (OC)	Weymouth	Oxfordian	D2	Durdle Door
Gault Clay (GC)		Albian	D3	Durdle Door
Nothe Clay (NC)	Osmington Mill	Oxfordian	D4	Durdle Door
Purbeck Shale (DD)	Durdle Door	Tithonian		

**Table 1.** Table showing the rock samples and oil seepages locations.

oil-stained shale. The D2 and D3 are taken from the same limestone bed with a 10 cm distance between them.

### Laboratory Work

#### Sample Preparation

The samples were left to be dry completely in order them to be ready for geochemical analysis. Then the samples were cleaned by using pentane; the tubes and tools were cleaned by DCM/pure. MeOH is used for dissolving water. Oil seeps were not subjected to cleaning because it may result in loss of hydrocarbon. Then all the rock samples and oil seepages were crushed into powder then were put the tubes in order to be ready for extraction.

#### Bitumen Extraction

For the extraction processes, 1-1.5 grams of the crushed samples were first put into labelled test tubes. Then 5 ml of Dichloromethane - Methanol (DCM/MeOH) 95:5 (v:v) was added into each tube. After that, the samples were put onto sonication for three minutes followed by the centrifuge for 5 minutes on 2000 rpm. With a pipette all the liquid were drained into another clean test tube without disturbing the solid part at the bottom. From the beginning all the steps were repeated three times. The activated copper grains particles were then added into the liquid samples in order to remove sulphur element within the samples.

#### Column Chromatography

Column Chromatography is a procedure used for fractionation samples into saturates, aromatics and polars in order to use for Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Before starting to the processes, the silica gel was activat-

ed by heating it at the temperature of 450 C for 2 hours. Meanwhile, the columns were prepared for further work. Quartz wool was first cleaned by using DCM and then plugged at the tip of each column in order for the solvent that was going to be put in to pour out of the column. After that, activated alumina gel was added to the column at about 1-1.5 cm high. Three clean labelled tubes were prepared for each sample: Saturates, aromatics and polars. 5 to 6 ml of Hexane is used for saturates, 5 to 6 ml. of DCM/Hexane 1:1 (v:v) for aromatics and 5 to 6 ml. of DCM/Methanol 1:1 (v:v) for polars is used to attain three different fractions. The first fraction is for saturate hydrocarbons or aliphatic hydrocarbons; second is for aromatic hydrocarbons and the third one is for polars (asphalt) compounds. Then the excessive amount of DCM is evaporated by using nitrogen gas. Then the proper amount of the solvents is poured into the labelled vials, and then they were sealed for the Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

#### Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography (GC) divides complex mixture into smaller, individual compounds and then transfers them into a mass spectrometry (MS) for detection and identification of the samples. Mass spectral characterisation was performed in full scan detection (m/z 50-550) using Selected Ion Monitoring (SIM). A splitless injection (1.0  $\mu$ l) GC-MS with an Agilent 6890 gas chromatograph (GC) and Agilent DB-5 column (30 m x 250  $\mu$ m x 0.25  $\mu$ m) was used with helium as a carrier gas. The oven temperature was initially held at 40 °C for 2 minute then 5 °C/min to 310 °C for 14 min. Mass spectra, the NIST mass spectral database, relative retention

times, and literature data have been used for identification of the compounds.

### Peak Identification

Two sets of fractions were recorded by the GS-MS: aliphatic and aromatics. Hopane and sterane distributions ( $m/z$  191 and 217 ions) were analysed for aliphatic fractions and the peaks were identified by using the 'MSD Chem Station' software (See Appendix 1 for the list of the peaks identified).

## GEOLOGY REVIEW

### Stratigraphy of the Basin

The stratigraphy and sedimentology of the Wessex Basin have been studied by several authors (e.g. Strahan 1920; Arkell 1947; Falcon and Kent 1950; Philips 1964; Dewey 1982; Stoneley 1982; Chadwick 1985). The Wessex Basin contains Palaeozoic, Mesozoic and Cenozoic sediments that have been deposited with an average thickness of approximately 1500 meters. In some locations this thickness exceeds 3500 m within the basin (Karner et al 1987).

### Tectonic Evolution of the Wessex Basin

Hawkes et al. (1997) suggested that there are four main tectonostratigraphic sequences that have modified the Wessex Basin, namely Early Atlantic, Atlantic, Biscay and Alpine.

#### a) Early Atlantic: Late Permian-Triassic:

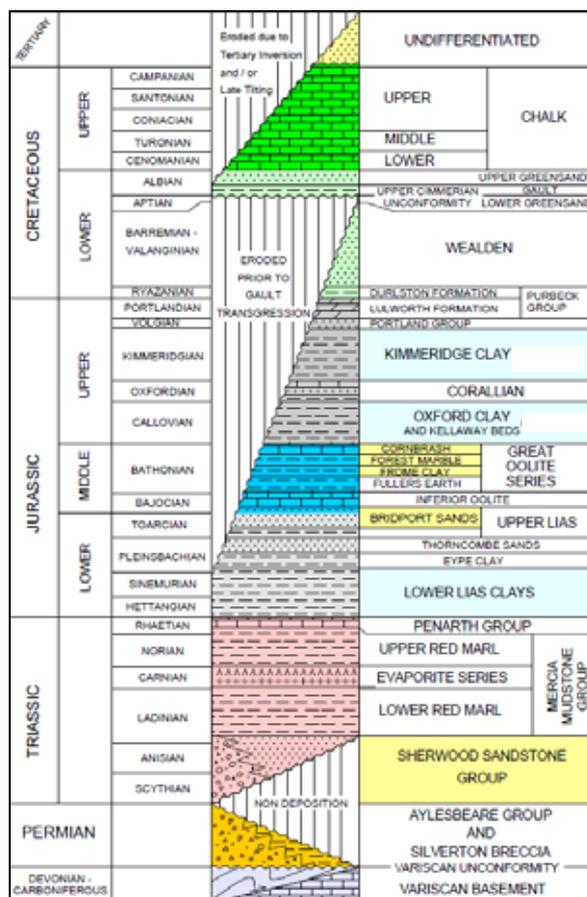
This sequence is defined by two fining-upward cycles. These cycles consist of continental clastic facies overlain by playa facies, all related to failed rifting of North Atlantic.

**b) Atlantic: Triassic-Late Jurassic:** This sequence is characterized by successful rifting in the central Atlantic. It contains a number of upward shallowing facies which led to formation of several source-seal-reservoir intervals. Source rocks such Blue Lias, Kimmeridge and Oxford Clay and reservoir rocks such Bridport Sands and Cornbrash Limestone located in this sequence. Other characteristics of this sequence are extensional faults and rotated fault-blocks which occurred during the rifting (Figure 6).

**c) Biscay: Late Jurassic-Late Cretaceous:** It is characterized by the successful rifting of the Bay of Biscay. Non-marine facies are observed in this sequence such as the Purbeck Formation and the fluvial deposits of Wealden formation. Howev-

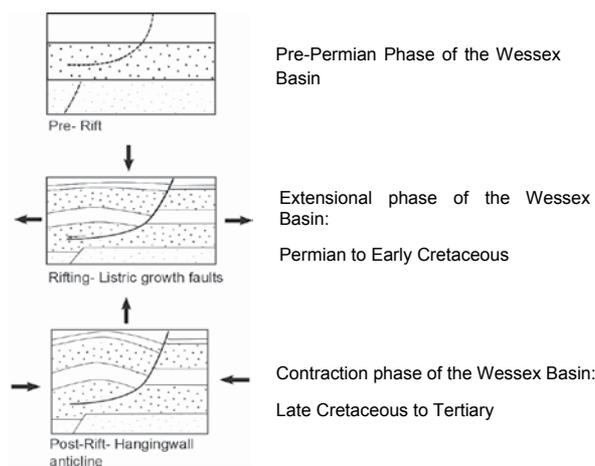
er, shallow marine deposition of Upper Greensand and the Chalk also occurred as a result of the Lower Cretaceous tilting and erosion.

**d) Alpine: Late Cretaceous-Tertiary:** North-south compression, which is related to the closure of Tethys and the Alpine orogeny, led to the re-activation of existing extensional faults. As a result, inversion of many basins and inverted anticlines in the hanging walls of existing faults occurred in



**Figure 6.** Stratigraphic column of the Wessex Basin showing the source rock (blue) and reservoir (yellow) (Modified from DTI, 2003 and West, 2009).

the region (Figure 7). This inversion resulted in destroying several cap rocks and escaping of hydrocarbons from earlier traps since it allowed faults to reopen. It also caused uplifting of mature source rock allowing them to cool down and stop expelling petroleum.



**Figure 7.** Schematic diagram for the tectonic phases of the Wessex Basin. (Modified from Smith & Hatton, 1998).

### Previous Geochemical Studies on Mesozoic Shales in the Wessex Basin

#### Liassic Shales

The geochemistry of the Liassic Shales has been studied in detail by many authors (e.g. Scott & Colter 1975; Butler & Pullan 1990; Hawkes et al. 1998; Ainsworth et al 1998). Ebukanson & Kinghorn (1985) stated that the Lower Lias shales have a TOC value of 7.36% at Charmouth and about 6 % at Lyme Regis. In Henfield-1, the TOC of the Lower Lias reaches a maximum of 2.5 % and a maximum vitrinite reflectance of 0.62 % Ro. In the Arreton-2 well, vitrinite reflectance values for Lower Lias range between 0.3 and 0.9% Ro (Ebukanson & Kinghorn, 1986a) and in the Penshurst-1 well it is 0.85% Ro. Penn et al. (1987) stated that the TOC of Lower Lias is up to 7% in the Dorset vicinity. McLimans & Videtich (1987, 1989) published a vitrinite reflectance map for the Lias in the Late Cretaceous. From the research, vitrinite reflectance values for the Blue Lias ranges between 0.7-0.9 % Ro. According to these authors, the Liassic Shales are the main source rocks of the Wessex and Weald oils. Ebukanson & Kinghorn (1990) published TOC values for Mesozoic shales in southern England, which are: Lower Lias, max. 7%; Kimmeridge Clay, max. 20%; and Oxford Clay Formation, max 12.36%. In-house studies, however, found TOC values of up to 7.8% in the Blue Lias of Lyme Regis (F. Spathopoulos, personal communication). In Dorset the laminated shales within the Blue Lias have average TOC values of 2 % and a maximum of 18% (Cornford, 1998). Scotchman (2001) stated that the Blue Lias in the Kimmeridge-5 well has a TOC range

between 1.1-1.5%. In Charmouth (Dorset) Liassic Shales have a TOC of 4.6-7%.

#### Oxford Clay

The Oxford Clay has TOC value of 12.3% and maximum vitrinite reflectance (VR) of 0.44 % in the Chickerell-1 well, VR of 0.42% Ro in Cranborne-1 well and 0.74 in Penshurst-1 well. (Ebukanson & Kinghorn, 1985). The Oxford Clay has a TOC of 12% in its lower part, which consist of bituminous shales and only 1% in its upper part comprising calcareous mudstone and limestones. According to Ebukanson & Kinghorn (1985), the Oxford Clay generated oil within the Weald Basin. Butler & Pullan (1990) pointed out that the Oxford Clay oil maturity peaked in Late Cretaceous. Finally, according to England (2010) the Oxford Clay in the Wessex basin is immature with a maximum vitrinite reflectance of 0.58.

#### Kimmeridge Clay

Ebukanson & Kinghorn (1985) stated that the Kimmeridge Clay has TOC values up to 20% in the Dorset area, with a maximum VR of 0.48% Ro. Ebukanson & Kinghorn (1986a) measured vitrinite reflectance values of 0.6% Ro in the Penshurst-1 well. Burwood *et al.* (1991) stated that the Kimmeridge Clay is in the oil window in the deep part of the Weald Basin. Buchanan (1998) pointed out that the Kimmeridge Clay is immature in the Wessex Basin and Hawkes *et al.* (1998) supported him, by claiming that the Kimmeridge Clay is immature over the whole of southern England. Lewan & Hill (2006) reported that the Blackstone Member of Kimmeridge Clay has TOC of 54%; Tmax of 409; and Hydrogen Index (HI) of 604. Based on its geochemical parameters, the Kimmeridge clay is, thus, the best potential source rock within the region.

#### Other Potential Source Rocks

In-house studies have shown that the Gault Clay has a TOC of 0.56 % and a HI of 66. The Nothe Clay has a TOC of 1.72% and a HI of 185. The Purbeck Black Shales have relatively high TOC and HI values with 5.36% and 1251 respectively.

#### BASIN MODELLING

In hydrocarbon exploration, it is essential to determine the maturity and petroleum potential of source rocks. For this purpose, 1-D Basin Modelling (using the Schlumberger's *PetroMod* software) was carried out in seven wells: (1) Wytch Farm B7,

(2) Wareham C3, (3) Lytchett 1, (4) Chickrell-1, (5) Bransgore-1, (6) Arrenton-2 and, (7) Lulworth Banks (Figures 1.3). The well Portsdown-1 in the Weald Basin was used for calibration, as it has vitrinite reflectance values. Estimated VR values from Ebukanson & Kinghorn (1985) were also used for calibration.

**Data Input**

**Main Input**

The lithology and depth data for the wells were acquired from the UK Onshore Geophysical Library (Figure 8). Total Organic Carbon (TOC), Hydrogen

Index (HI) and other source rock properties used for the modelling were sourced from British Geological Survey (BGS) and previous studies, such as Ebukanson & Kinghorn (1985); Ebukanson & Kinghorn (1986a) and Ebukanson & Kinghorn (1986b).

**Basin Heat Flow**

Karner et al. (1987) suggested that subsidence in the Wessex Basin occurred during a regional thermal subsidence, punctuated by a number of rapid, finite, renewed subsidence events, indicating a “polyphase” extension. Each stretching event was predicted to initiate a major period of clay deposi-

Layer	Top [m]	Base [m]	Thick. [m]	Eroded [m]	Depo. from [Ma]	Depo. to [Ma]	Eroded from [Ma]	Eroded to [Ma]	Lithology	PSE	TOC [%]	Kinetic
Eroded	0	69	69	70	50.00	0.00	50.00	0.00	Sandstone (typical)			
Chalk	69	257	188	500	95.00	70.00	70.00	50.00	CHALK			
U.Greensand/Gault	257	345	88		100.00	95.00			SANDshaly			
L.Greensand	345	373	28	75	120.00	105.00	105.00	100.00	SANDSTONE			
Wealden	373	625	251	750	140.00	125.00	125.00	120.00	SILT&SAND			
U.Purbeck	625	689	64	100	147.00	145.00	145.00	140.00	LIMESTONE			
Portland	689	713	24	0	152.00	150.00			LIMESTONE			
Kimmeridge Clay	713	1049	336	0	156.00	154.00			SHALE	Source Rock	4.00	Pepper&Corv
Corallian	1049	1084	34	0	160.00	157.00			SAND&LIME			
Oxford Clay	1084	1233	149	0	164.00	161.00			SHALE	Source Rock	1.50	Pepper&Corv
Great Oolite	1233	1369	136	0	168.00	167.00			LIMEsandy			
Inferior Oolite	1369	1487	118	0	175.00	170.00			LIMEsandy			
U.Lias	1487	1573	86	0	183.00	179.00			SHALE			
M.Lias	1573	1660	87	0	188.00	184.00			SHALE			
L.Lias	1660	1905	244	0	200.00	188.00			SHALE	Source Rock	0.90	Pepper&Corv
Rhaetic/Penarth	1905	1925	20	0	203.00	200.00			SHALEcarb			
Mercia Mudstone Group	1925	1930	5	0	237.00	203.00			SHALEsilt			
Devonian	1930	2105	175	0	240.00	237.00			SHALEsilt			

Figure 8. Main input data for Portsdown-1 well. All the data was obtained from BGS.

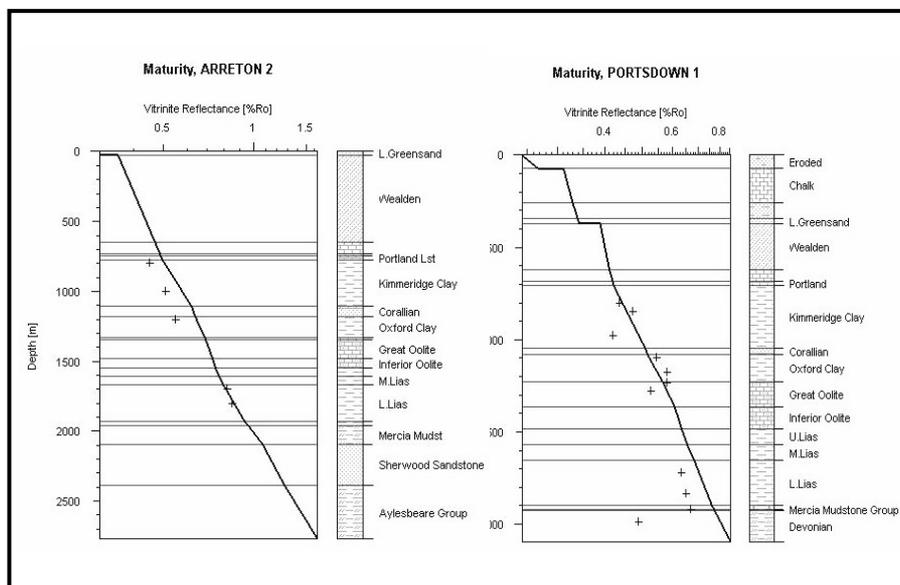


Figure 9. Calibration wells: Arrenton-2 and Portsdown-1. The diagram shows that the modelled VR values matches with the calculated VR and VR values from the well. Portsdown 1 well is located on the Weald Basin being 2 km away from the Arrenton-2 well.

tion and to contain two phases: (a) an active rift, or *mechanical* phase (from 10 to 50Ma) and, (b) a passive, *thermal* phase (80 to 200Ma) (Karner et al. 1987).

For calibration, the well Portsdown-1 was used within the Weald Basin as it has VR values for the source rocks. It is located 2-3 km to northeast of Arrenton-2 well. Also, estimated VR values from the Ebukanson & Kinghorn (1985) were used for calibration Arrenton-2. These seven wells are also used for the modelling in order to determine mature source rock kitchen (Figure 5.2).

**Paleowater Depth (PWD) and Sediment-Water Interface Temperature (SWIT)**

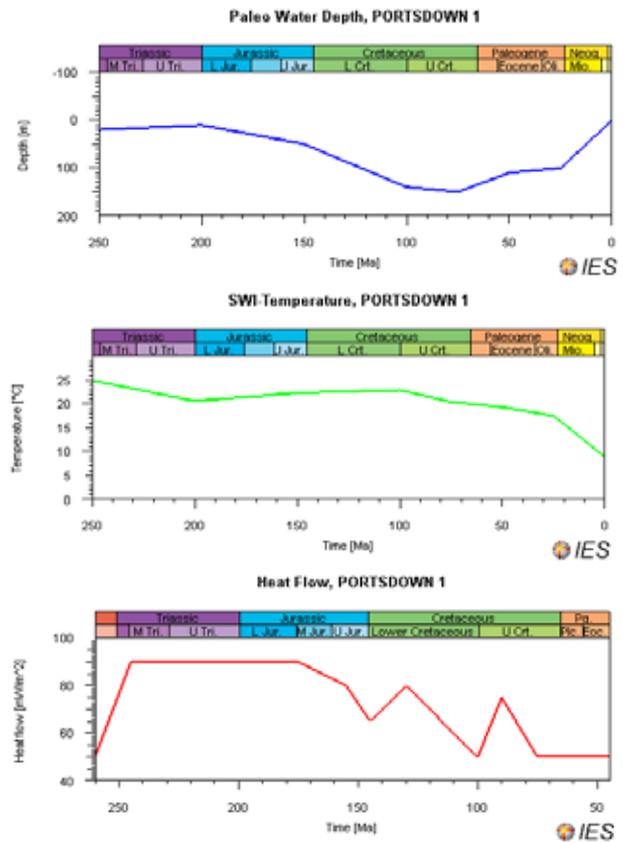
Paleowater Depth data was calculated from a relative sea level curve (Ainsworth et al., 1998) and from the well lithology (Figure 10).

**Erosion Thickness**

The estimate erosion thicknesses of strata were derived from the publications of Law et al. (1998) and Butler et al. (1998) and also from the regional stratigraphy. Since the hanging walls of the Purbeck and Abbotsbury-Ridge Faults have effected from the Tertiary inversion, it is crucial to create restore maps or cross-sections in order to model the wells that are located on. Thus, the restore cross-sections from the Underhill & Stoneley (1998) were used for the study.

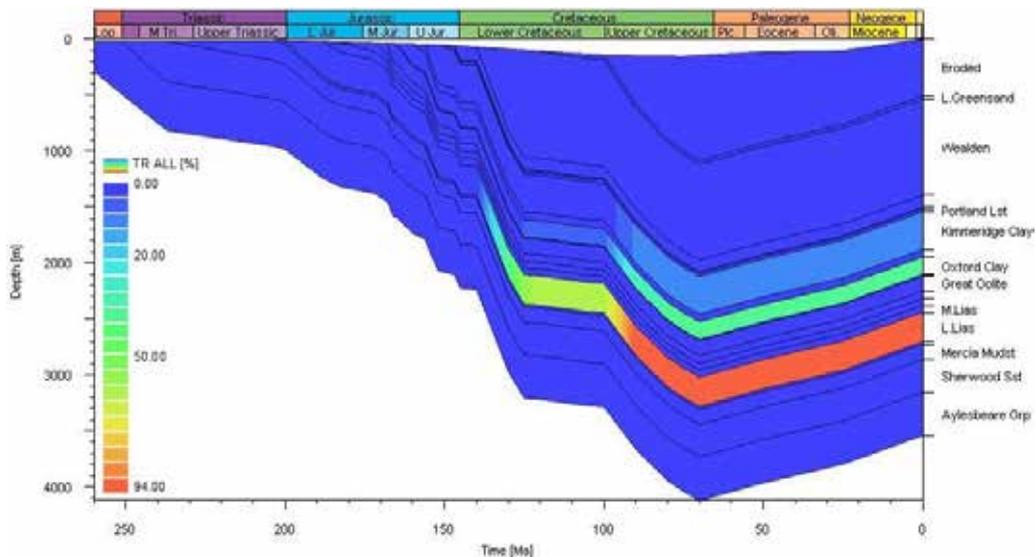
**Burial History**

Burial history diagrams obtained from the ba-

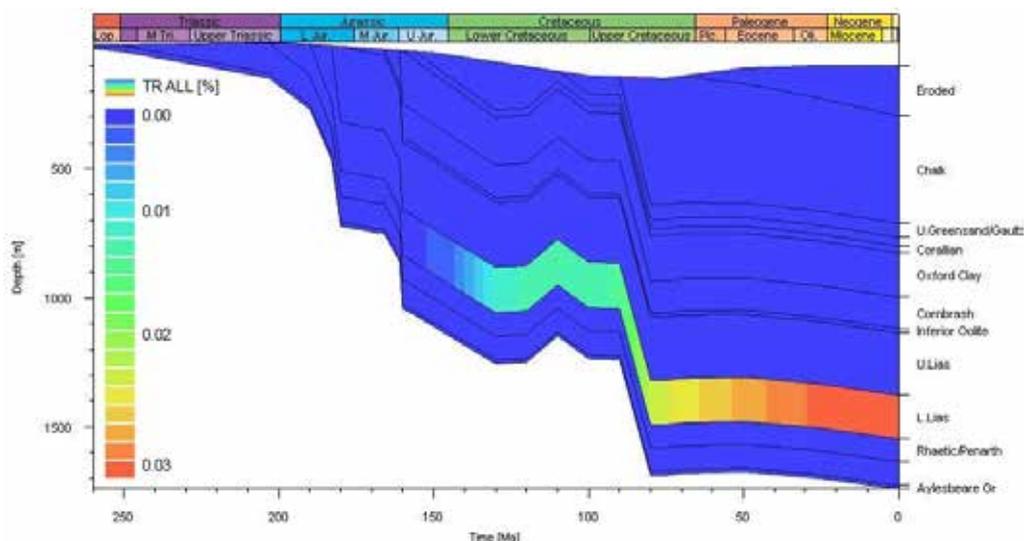


**Figure 10.** Boundary conditions for Portsdown 1 well showing the input data for PWD, SWIT and Heat flow which are calibrated with the VR values of the same well.

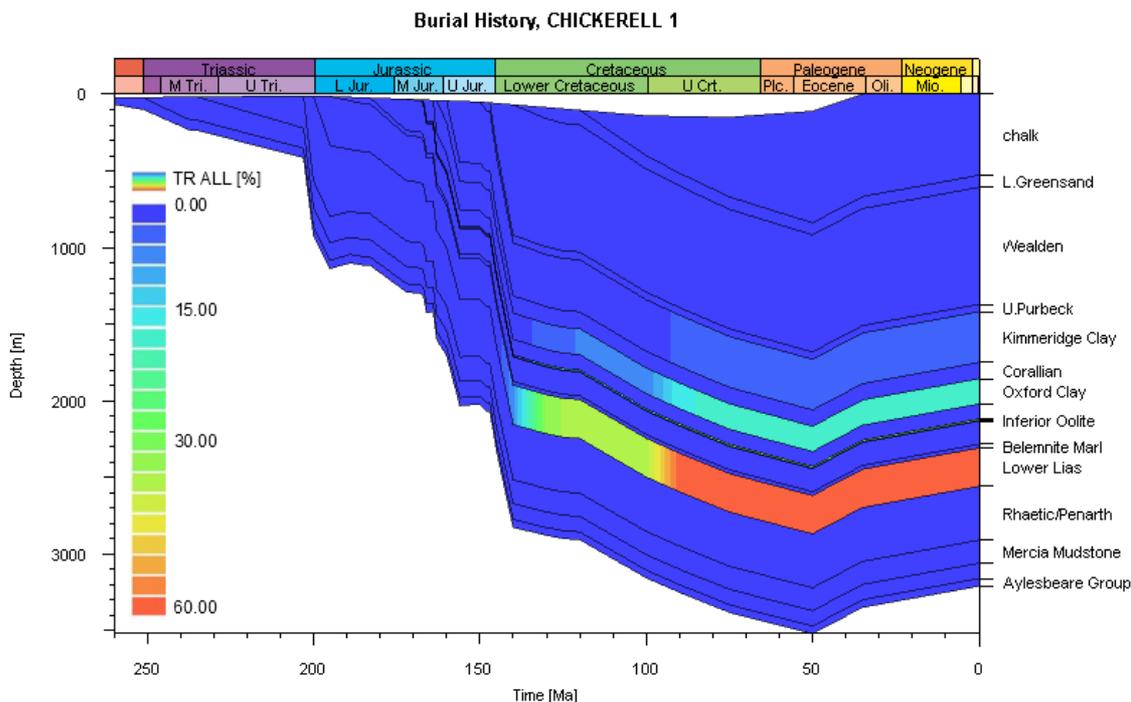
sin modelling indicate that only in the Arrenton 2, located in the hanging wall of Purbeck Fault, and the Chickerell-1, located in the hangingwall of the



**Figure 11.** Burial history for Arrenton-2 with overling TR values. The Lower Lias has a TR value of up to 94. The Oxford Clay about 50 %, on the generation threshold.



**Figure 12a.** Burial history for Bransgore-1 with overlying TR values. The well is located on the footwall of the Purbeck Fault. The figure shows that all the potential source rocks are immature with the TR values lower than 1%.



**Figure 12b.** Burial history for Chickerell well with overlying TR values. The TR values suggest that the Oxford Clay is immature with a TR value of 15% while the Lower Lias is mature with 60% TR.

Abbotsbury – Ridgeway Faults, the Liassic source rock was buried enough to generate hydrocarbons. As shown in the model, the Lower Lias shales were buried up to 3000 m, enabling them to generate and expel hydrocarbons (Figure 11). The Oxford Clay in this well is in the threshold of generating oil. In the other wells the potential source rocks were not buried enough to become mature (Figure 12).

According to the above observations, therefore, the Lower Lias shale is mature if the source rock is located to the south of the Purbeck-Isle of Wight disturbance, where the strata were buried deeper than in the northern part of the Disturbance, due to displacement of the two major faults in the area: the Purbeck and the Abbotsbury-Ridgeway Faults.

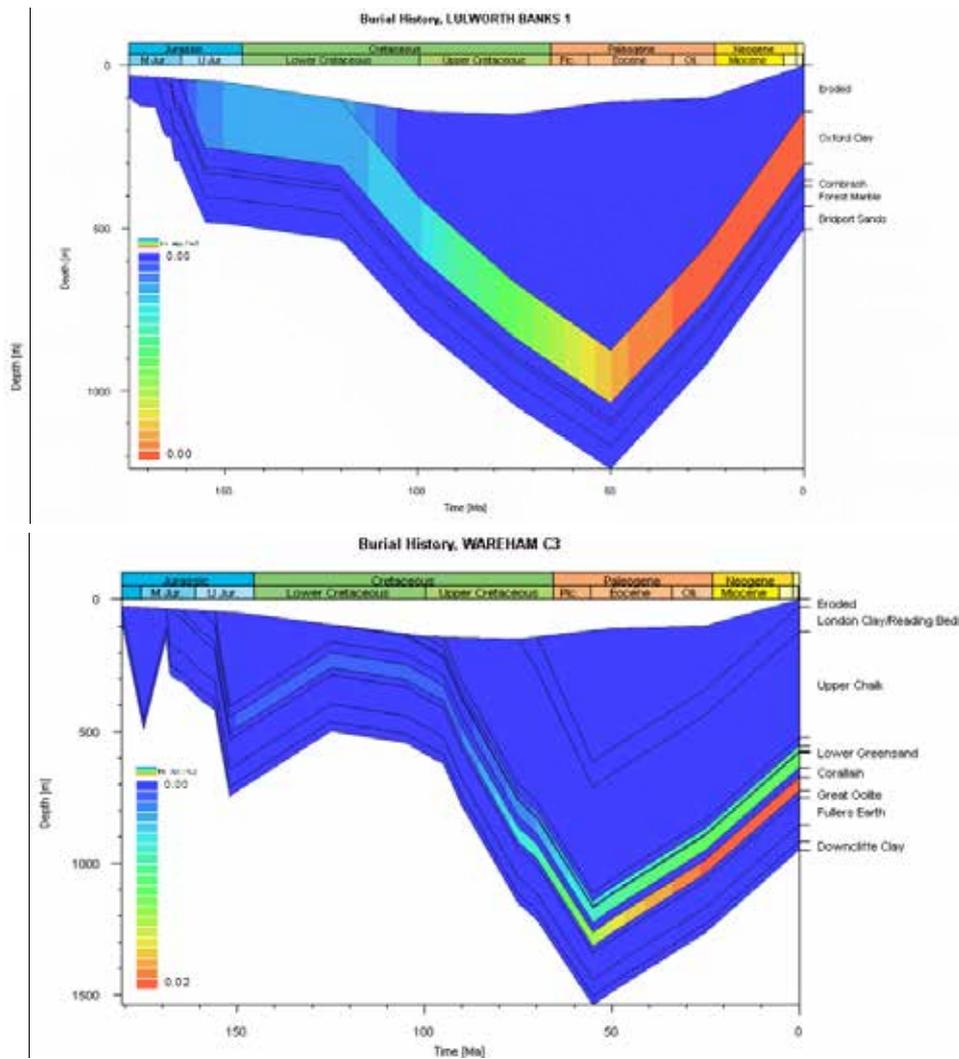


Figure 13. Burial history diagrams for Lulworth Banks and Wareham C3 wells with overlying TR values.

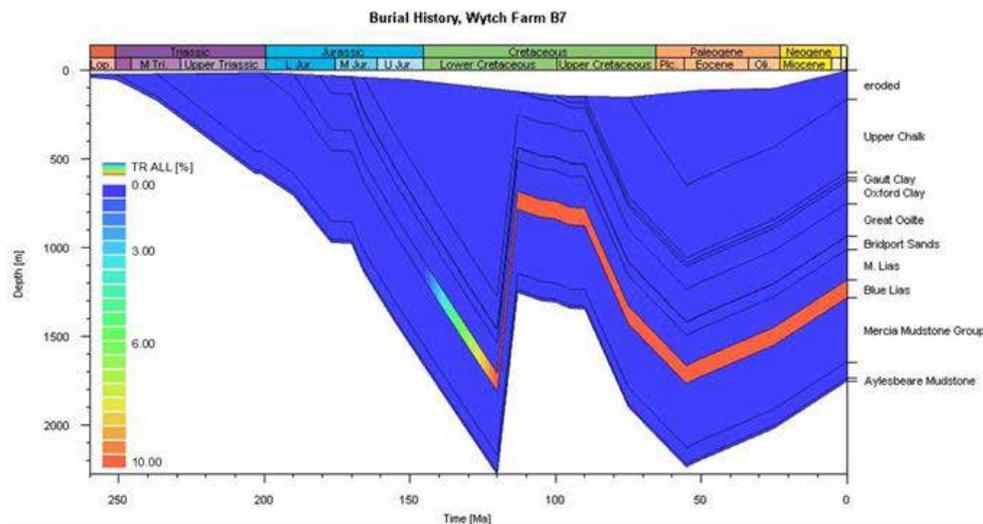


Figure 14. Burial history for Wytch Farm B7 well with overlying TR values. The Lower Lias has a TR value of up to 10 %, suggesting that the source rock is immature in the Wytch Farm oilfield area.

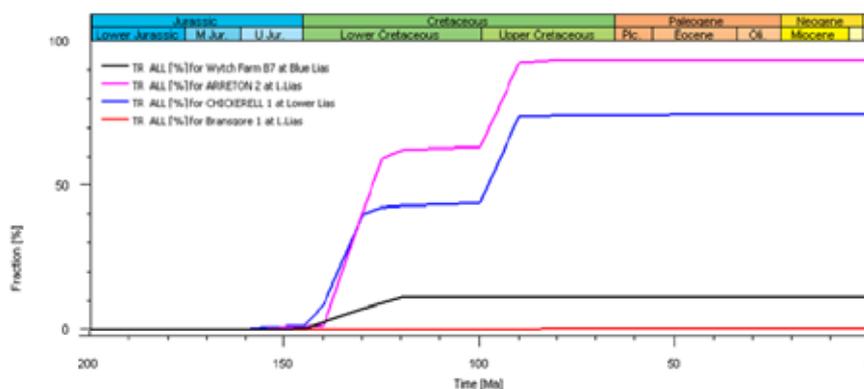
### Source Rock Maturation

The maturation of the Mesozoic source rocks across the Wessex Basin was determined by 1D basin modelling. The transformation ratio (TR) values (i.e. ratio of transformed kerogen to petroleum vs immature kerogen) for source rocks increase with maturity.

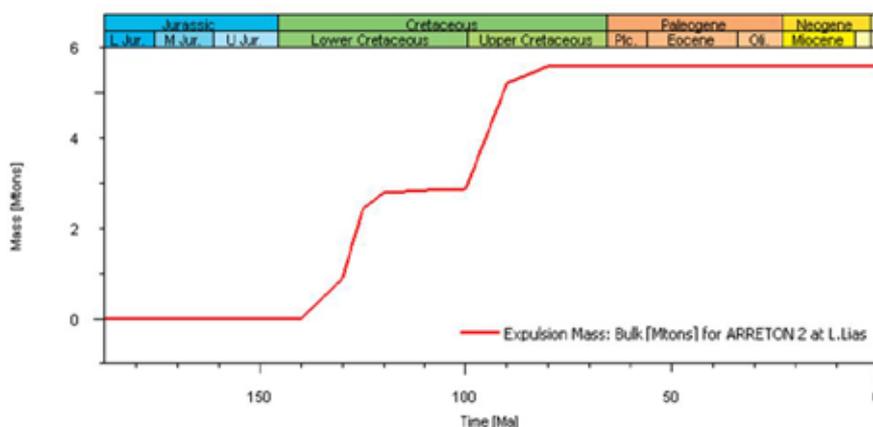
Based on the modelling results, the Lower Lias is mature only in the wells Arrenton-2 and Chickrell-1. In these wells TR values for the Lower Lias is up to 94% and 60% respectively (Figure 15). In the other wells the Lower Lias is immature even in the Wytch Farm vicinity (Well Wytch Farm D5). The TR vs Time plot for the Lower Lias in these wells show that oil generation lasted from the Early Cretaceous until the Late Cretaceous. In addition to the Lower Liassic, the Oxford Clay is about to enter oil window in these two wells. The Kimmeridge Clay, however, is immature in the all wells (Figure 16). The expulsion vs plot suggests that the Blue Lias in Arrenton-2 had expelled over 5 Mtons of hydrocarbons during the Cretaceous times while the Oxford Clay had ex-

pulsed about 0.7 Mtons of hydrocarbons during the Late Cretaceous in the same well (Figure 16 and 17).

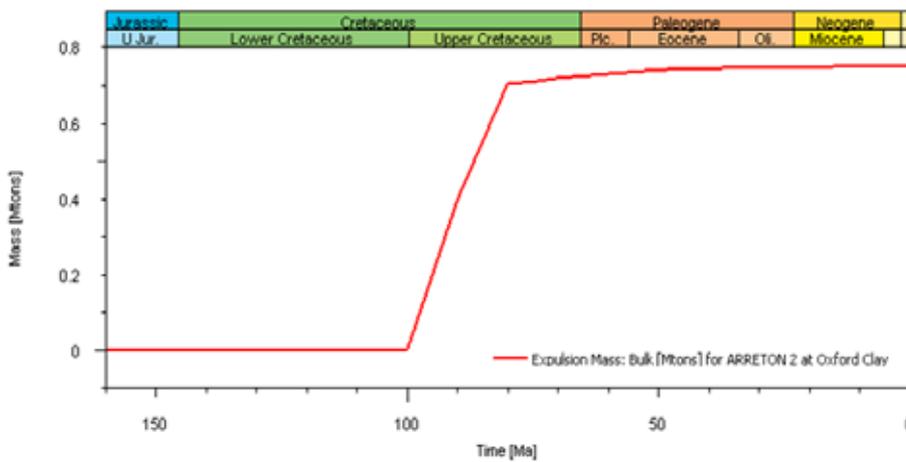
The wells in which the source rocks are mature are in common that they both are located on the hangingwalls of the two major faults: Purbeck Fault and the Abbotsbury-Ridgeway Fault. This enables the source rocks to be buried enough to transform the kerogen into the hydrocarbons. They were then accumulated within the traps to the north probably by lateral and vertical migration. Because oil-source correlation from the geochemical analyses shows that the oil in the seepages might source from the Lower Lias. Thus, this requires a N-NW migration from source to the seepages or to the traps, in other words a migration from the hangingwalls of the faults to the footwalls. In the wells that are located in the footwalls, however, the potential source rock could not burry enough to generate hydrocarbons, probably because the area was effected by the Early Cretaceous uplift and Tertiary inversion.



**Figure 15.** TR values for 4 wells showing that the Lower Lias started hydrocarbon generation in the Early Cretaceous and peaked in the Late Cretaceous. After the Late Cretaceous there is no oil or gas generation took place.



**Figure 16.** Expulsion vs Time plot for the Blue Lias in Arrenton-2 well. The figure shows that the Blue Lias had expelled over 5 Mtons of hydrocarbons during the Cretaceous times.



**Figure 17.** Expulsion vs Time plot for the Oxford Clay in Arreton-2 well. The figure shows that the Oxford Clay had expelled about 0.7 Mtons of hydrocarbons during the Late Cretaceous times.

**PETROLEUM GENERATION AND MIGRATION**

**Relative Timing of Migration and Generation**

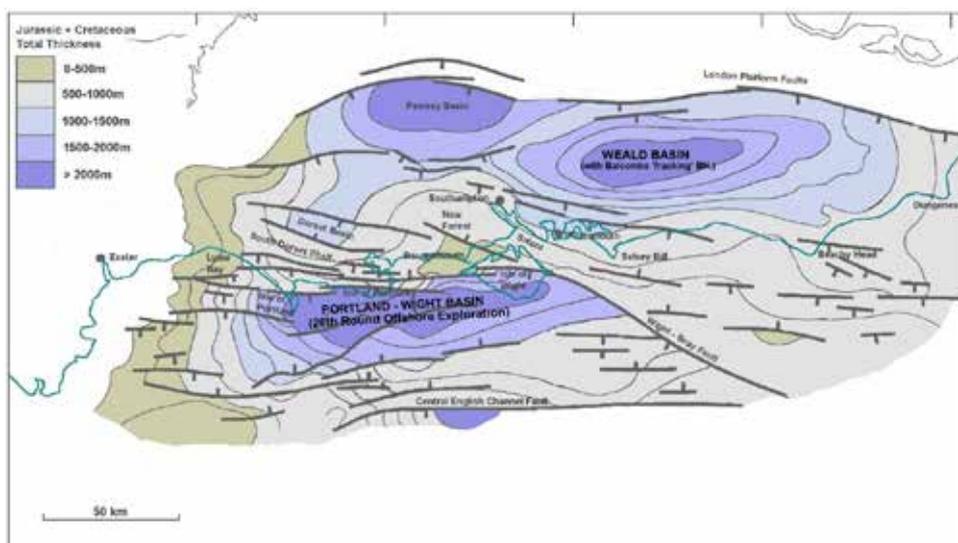
Although, it may be the most crucial issue for the future hydrocarbon exploration of the Wessex Basin, the timing of generation and migration of hydrocarbons in this basin has been a subject of controversy due to the complex tectonic history of the basin.

The Mupe Bay oil seep is a key evidence to constrain the timing of hydrocarbon migration in the Wessex Basin. Both the clasts and the host rock (matrix) of the Lower Cretaceous sandstone in the Wealden Formation are stained by oil. There is a maturity difference between the oils in the clasts and matrix (Selley & Stoneley, 1987; Cornford et al., 1988; Kinghorn et al., 1994; Wimbledon et al.,

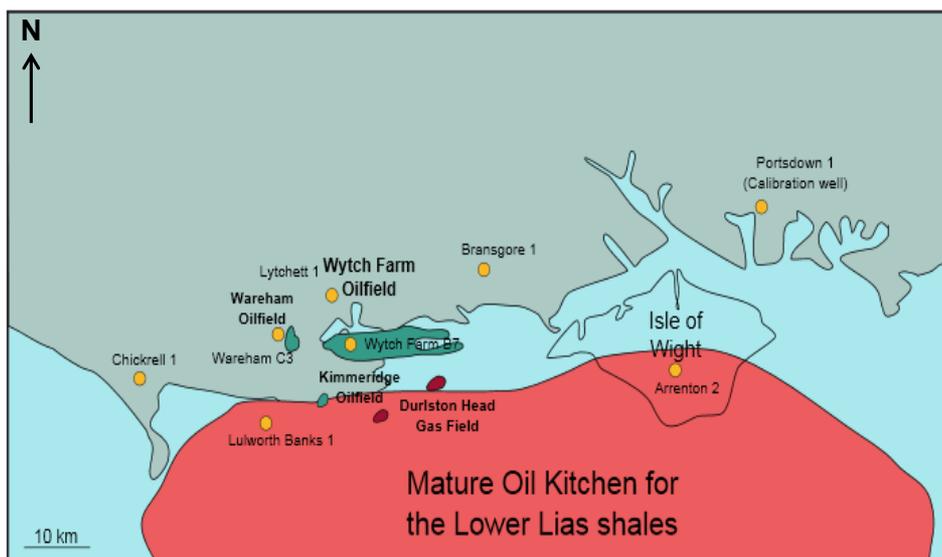
1996). Two hypotheses were proposed: (a) the clast and matrix were stained at the same time; or (b) in different times (i.e. single-phase staining mechanism versus two-phase staining mechanism).

**a) Single-phase staining mechanism:** In this hypothesis, both the clasts, which made of the stained rock in Wealden Formation, and the matrix itself were stained by oil at the same time. The maturity differences between clasts and matrix can be explained by biodegradation heterogeneity. Because rocks or clast with different porosity and permeability can be subjected to different level of biodegradation; thus, different level of maturities.

**b) Two-phase staining mechanism:** According to this hypothesis, clasts and the matrix were stained in different times. First, the clasts which are older than the rock itself were stained by early ma-



**Figure 18.** Isopach Map showing Main Jurassic and Cretaceous sedimentary depocenters. From Ian West (2013).



**Figure 19.** Schematic diagram showing the oil kitchen area for the Lower Liassic Shale based on the Basin Modelling. (Modified from Ian West and Tonya West, 2008) Note that the boundary of the kitchen is very approximate.

ture oil, generated in the Early Cretaceous. Later, the rock matrix consisting these clasts were subjected to stain by fairly mature oil, generated in the Late Cretaceous. The Blue Lias shales were generating oil starting from the Early Cretaceous based on this hypothesis.

A new study showed that the clast and the matrix are different in magnetic directions, indicating that the oil in the clast and in matrix came in different times, proving a two-phase oil staining. This model suggests that the oil was already being generated and was migrating by the Early Cretaceous (Emmerton S., Muxworthy A. R. and Sephton M.A. 2013). Selley & Stoneley (1987) also support the two-phase oil staining model. Stoneley (1992) stated that the Lower Lias reached the maximum maturity in the Late Cretaceous. However, the seepage in the Mupe Bay suggests an earlier oil generation by the Early Cretaceous.

Ebukanson and Kinghorn (1986a) stated that, in the Wytch Farm oilfield, the oil in the Sherwood Sandstone and the Bridport Sands came from the same source rock, the Blue Lias. The oil probably migrated from the south of the Purbeck-Isle of Wight Disturbance, where the Lower Lias was buried deeply enough, thus is mature (Figure 18). In the Kimmeridge oilfield, the source rock is also the Lower Lias shales (Selley & Stonely 1987).

### Migration Pathways

The migration pathways within the Wessex Basin are also a subject of discussion. This may be be-

cause complex migration pathways and mechanism are required in order to move petroleum from the Liassic source rock, located to the south of the Purbeck-Isle of Wight Disturbance, into the carrier beds such as Triassic Sherwood Sandstone and Jurassic Bridport Sands.

A number of wells were proven to be unsuccessful because they were drilled on the structure that either they never accumulated hydrocarbons due to timing or that they were never on the migration pathway. This reveals the importance of understanding the timing and migration pathways within the Wessex Basin (Hawkes et al, 1998). The exploration success of specific structures within the basin depends on the timing of hydrocarbon generation, migration and trap formation and their relative order to each other.

One of the major issues in terms of migration is the movement of oil from the Liassic source rock into the stratigraphically older Triassic Sherwood Sandstone reservoir. A probable model is that the faulting caused to the juxtaposition of the source rock and the reservoir (Figure 20). It must be noted that for the Bridport Sandstone a fault movement may not be required, as the reservoir overlies the Liassic source rock. A simple *vertical* migration with a relatively short *lateral* migration could be a good explanation for the hydrocarbon movement from source rock into the carrier beds (Figure 21). Predicting areas where such juxtaposition may have occurred are important in terms of future exploration in the Wessex Basin. The Tertiary inversion makes

this prediction difficult, however, due to reverse movement of the existing faults.

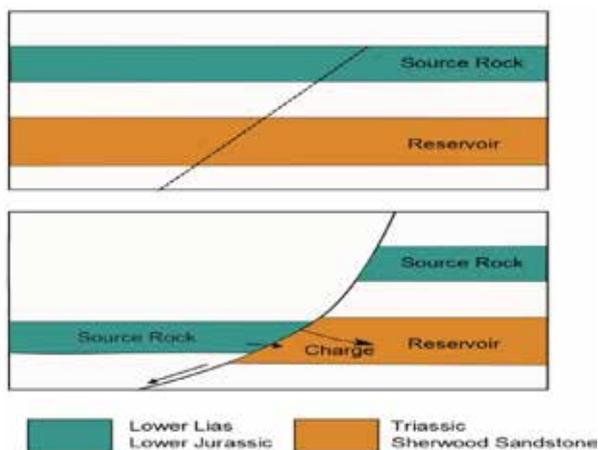
The Kimmeridge structure in Kimmeridge oilfield is called 'Lone Survivor', as it is the only one which preserved oil during the Tertiary uplift, while other structures proved to be dry. There are two possible explanations for these dry wells: (a) the first one is that petroleum existed within the traps, but, after the uplift and disturbance of the structures, the oil escaped either to the surface, or towards other carrier beds; (b) the second explanation is that the oil never accumulated within these structures. Among these two possible explanations, the first one is believed to be more likely, based on the oil and gas seeps within the area and the oil shows from the wells such as Martinstown-1 and Arreton-2 on the Isle of Wight.

Previous studies, published isopach maps (Figure 18) and the basin modelling that was conducted in this study indicate that the kitchen for the Liassic source rock is located to the south of the Purbeck-Isle of Wight disturbance (Figure 19). This suggests that both vertical and lateral migrations must have occurred in the Wessex Basin. The position of the source rocks and reservoirs, as well as the active and fossil seepages along the fault planes vertically and laterally (Colter and Havard, 1981) conform to this model.

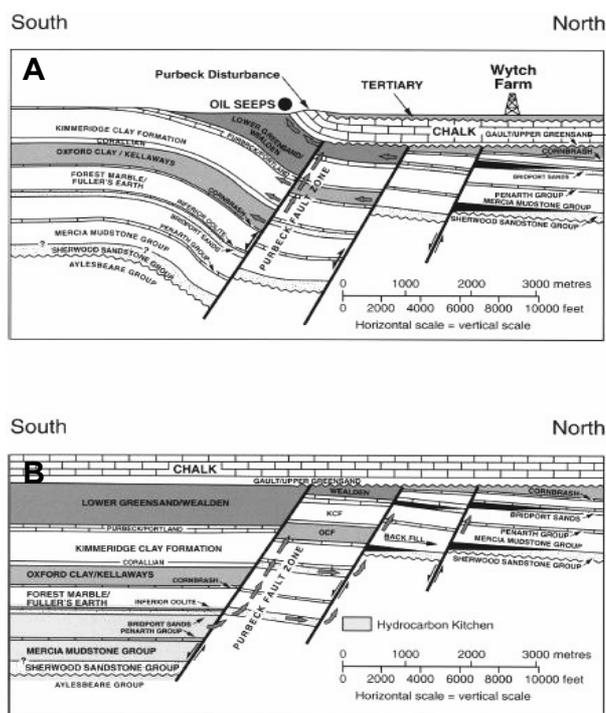
### Re-migration

Underhill & Stoneley (1998) stated that re-migration did not play a major role in the movement of hydrocarbons in the Wessex Basin. However, some structures which were modified by the Tertiary inversion such as the Kimmeridge closure, may have received the oil from a late generating source rock (the Lower Lias) or from limited re-migration from a pre-existing, breached traps. The latter theory is based on active oil seeps and the production of the Kimmeridge oilfield, which proved higher than was initially calculated.

Re-migration of hydrocarbons since the Miocene inversion is, also, suggested by breached accumulations on some surface features, indicated by oil shows, and the present day seeps/impregnations along the Dorset coast. Present-day seepages are very important for the identification of re-migration pathways. To date there has been no detailed study on re-migration pathways as it is believed that re-migration has not led to an important hydrocarbon accumulation.



**Figure 20.** Schematic diagram showing the possible explanation of the oil charge from the Lower Lias shales into the underlying Triassic Sherwood Sandstone. Half graben basin and juxtaposition of the Triassic reservoir and the Liassic source rock. (A) Strata before faulting (B) After faulting.



**Figure 21.** Cross-sections through Wytch Farm Oil Field showing hydrocarbon kitchen, plays and migration pathways. (A) Present Day; (B) Tertiary, before Alpine Orogeny. From Colter & Havard (1981).

## GEOCHEMICAL ANALYSES

### Extractable Organic Matter (EOM)

The table below summarizes the extractable Organic Matter (EOM) for 14 samples (range 0.15 – 0.85%). From the table, ST, MB, and OM (2ml) samples did not have powder because they have been taken from ST, MB, OM samples and been diluted for ease of analysis. 2 ml of the original extraction aliquot from three oil samples (ST, MB & OM) was taken to dilute with 8 ml of DCM. After well mixing of the sample and DCM, an aliquot of 2 ml from each sample (ST, MB, and OM) was separated in different tube and labelled, for example, ST (2ml). The negative value (-5.4) of BL2 sample indicates that there was an error in the measurement.

### Molecular Composition

All the rock and seep samples analysed shows that the normal-alkanes and isoprenoid alkanes have been biodegraded since they are more vulnerable to alterations compared to hopanes and steranes. However, steranes can be altered due to heavy biodegradations so extra care should be taken for the interpretations based on sterane distributions. Gault Clay sample (GC) has no biomarker so that the biomarker analyses for this sample could not be conducted. Moreover, D2, D3, D4, KC, MB, OM and ST samples contain tricyclic terpanes (C19-C27).

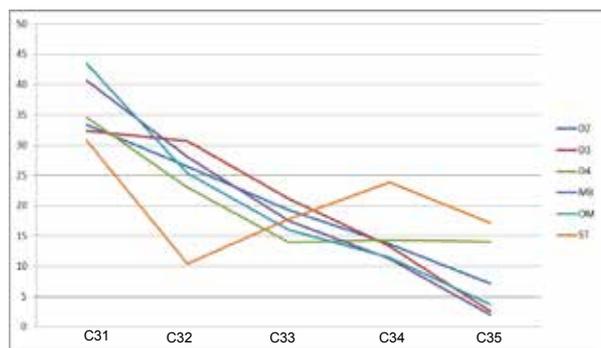
### Correlation of Oil Seeps

The relative distributions of C31-35 17 $\alpha$  (H), 21 $\beta$  (H) 22S and 22R homohopanes can be used as an indication of the relative origin of the samples. The homohopane distribution diagram (Figure 22) for the seep samples (D2, D3, D4, MB, OM and ST) shows that the curves are sub-overlapped with each other. This overlap explains that the the source rock that generated oil within these samples were deposited in similar environmental conditions. Peters and Moldowan, (1991) stated that the homohopane distribution can also be affected by the thermal maturity so that the curves also have maturity indication. While the C<sub>35</sub> homohopane index increases with increasing thermal maturity, C<sub>31</sub> index decreases (Peters and Moldowan, 1991). The diagram shows that the samples have similar value of C31 and C35 index which is likely for them to have similar maturities. However, ST samples has slightly different curve compared than other.

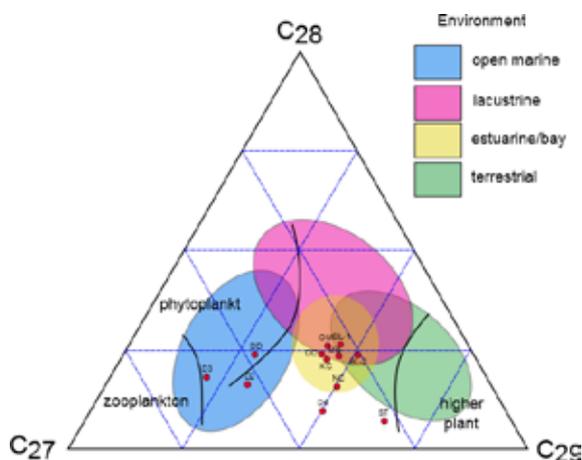
According to Ourisson (1979 & 1984) C31-C34 homohopanes comes from bacteriopolyhopanol of prokaryotic cell membrane while C35 homohopane may due to heavy bacterial activity. Peters and Moldowan (1991), on the other hand, pointed out that abundant C35 homohopane may be the indicators of highly reducing –low Eh- marine condition while low C35 concentration could be explain by oxidizing – high Eh- water condition.

Sample	Sample powder weight (g)	Weight of tube (g)	Weight of copper (g)	Tube+ Copper weight (g)	Extraction tubes weight (g)	EOM (g/g)	EOM (mg/g)	EOM (%)
GC	1.7937	7.7791	0.0725	7.8516	7.8531	0.0015	1.5	0.15
KC	1.6976	7.6572	0.0995	7.7567	7.7597	0.003	3	0.3
NC	1.8578	7.8734	0.0855	7.9589	7.9609	0.002	2	0.2
OC	1.6242	7.7105	0.0873	7.7978	7.8038	0.006	6	0.6
DD	1.8886	7.7992	0.0807	7.8799	7.8884	0.0085	8.5	0.85
BL1	1.6001	7.6758	0.1029	7.7787	7.7863	0.0076	7.6	0.76
BL2	1.6566	7.8027	0.0662	7.8689	7.8635	-0.0054	-5.4	-0.54
MB	1.7597	7.8261	0.0742	7.9003	8.023	0.1227	122.7	12.27
ST	1.6241	7.5929	0.0668	7.6597	7.7566	0.0969	96.9	9.69
OM	1.6268	7.5843	0.115	7.6993	7.8481	0.1488	148.8	14.88
D2	1.7031	7.7487	0.0757	7.8244	7.8375	0.0131	13.1	1.31
D3	1.5376	7.7553	0.0709	7.8262	7.8385	0.0123	12.3	1.23
D4	1.5617	7.743	0.1125	7.8555	7.8582	0.0027	2.7	0.27
ST(2ml)	0	7.738	0	7.738	7.7419	0.0039	3.9	0.39
MB(2ml)	0	7.7382	0	7.7382	7.7427	0.0045	4.5	0.45
OM(2ml)	0	7.7963	0	7.7963	7.8037	0.0074	7.4	0.74

**Table 2.** Table showing the extracted organic matter (EOM) from the analysed samples.



**Figure 22.** C31-35 17α (H), 21β (H) 22S and 22R homohopanes distribution diagram.



**Figure 23.** C27-C28-C29 sterane ternary diagram showing the depositional environment of the source rocks. After Shanmugam(1985) and Huang & Meinschein (1979).

**Depositional environment of source rocks**

Ternary diagram is used for determining the depositional environment of the source rocks. C27-

C28-C29 sterane ternary diagram (Figure 23) is divided into four main environments: open marine, lacustrine, estuarine and terrestrial. From the Figure 23 most of the samples are concentrated in a small area, in estuarine environment except ST, D2, D3 and DD samples. ST sample shows high concentrate of C29 while D2, D3 and DD samples shows high C27 sterane concentration.

Tricyclic terpanes also depositional environment indicators, which according to Aquino et. al. (1983) they are associated with marine source. They are also indicator of maturity (Van Grass, 1990). Hunt (1996) also stated that the tricyclic terpanes increases in dominance with increasing maturity.

**Maturation**

Maturation of crude oil is an important parameter for oil-oil and oil-source correlations. Biomarker maturity parameters Ts/Ts+Tm and 20S/(20S+20R) C29 sterane ratios are used in order to determine maturity of the samples (Table 3) The 20S/(20S+20R) C29 sterane is one of the most common molecular maturity parameters in petroleum geochemistry (Peters and Moldowan, 1993). From the table 3, the values for the 20S/(20S+20R) C29 sterane ranges from 0.12 to 0.82. The highest ratios belong to the seep sample while the lowest one is KC sample with 0.12. BL-1, BL-2 and OC samples are very close to each other with the maturity values of 0.28, 0.27 and 0.26 respectively, showing immaturity for these samples. NC is also immature (0.24) based on this maturity parameter.

Ts/Ts+Tm maturity parameter values vary between 0.39 and 0.78. The seep samples, again, have the highest values. BL-1, BL-2 and OC sam-

Sample	Ts/Tm	Ts/(Ts+Tm)	Hopane, C31 22S/(22S+22R)	Sterane, C29ααα 20S/(20S+20R)	Steranes (S+R) %C27 %C28 %C29		
OM	3.25	0.76	0.67	0.51	31.47	25.35	43.18
ST	3.46	0.78	0.74	0.82	29.12	7.80	63.08
D2	1.71	0.63	0.78	0.11	51.59	19.47	28.94
D3	2.14	0.68	0.86	0.74	65.47	16.17	18.37
D4	1.64	0.62	0.56	0.41	40.16	11.35	48.49
MB	2.03	0.67	0.62	0.47	29.86	24.05	46.09
BL1	0.66	0.40	0.36	0.28	32.05	22.97	44.99
BL2	0.62	0.38	0.32	0.27	27.78	23.12	49.10
KC	1.40	0.58	0.85	0.12	31.98	23.83	44.19
NC	0.64	0.39		0.24	34.26	15.59	50.15
OC	0.71	0.41		0.26	33.98	23.75	42.27
DD	2.09	0.68	0.13	0.14	48.08	22.85	29.07

**Table 3.** Table showing the biomarker maturity parameters and C27, C28, C29 Steranes.

ples have similar values for this parameter as well (0.40, 0.38 and 0.41 respectively). KC, however, has a value of 0.58, which indicates a higher maturity values compared to C29 sterane maturity parameter. It is because Ts-Tm indicator depends on not only thermal maturity but also source and oxidation. Based on these two biomarker maturity parameters only the oil-seep samples have mature signatures while the rock samples, however, are all immature.

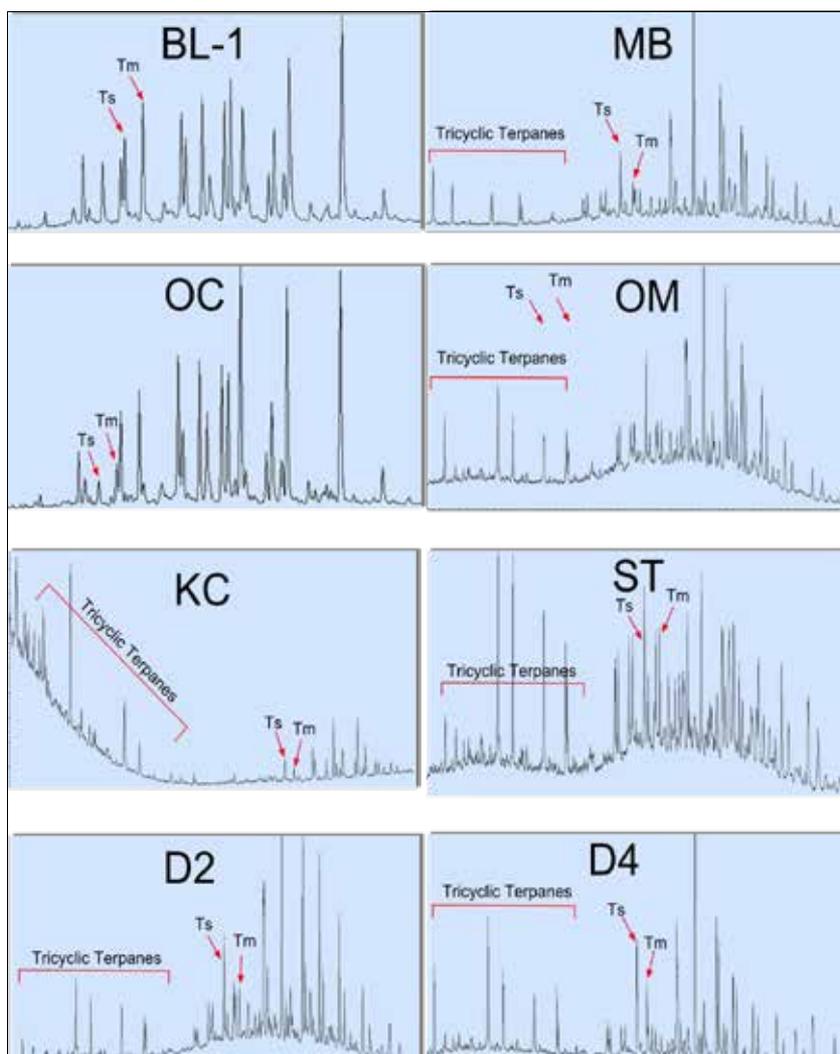
#### 1.4 Biomarker Abundance

Each sample has its own unique gas chromatogram distribution/pattern based on their biomarker content, thus this can be a guideline for maturity indication and oil-oil or oil-source rock correlation. The distribution patterns of OM, MB and ST, with some noise on ST sample (Figure 24). Likewise, D2, D3 and D4 samples have the similar pattern.

Among the rock samples, KC has a different pattern compared to BL and OC samples. BL-1, BL-2 and OC samples have very similar distribution patterns due to their biomarker content similarities.

#### Lithology of Source Rocks: Clay-rich vs Carbonate-rich

Source rocks can be divided into two categories: Clay-rich and carbonate-rich. Based on previous geological studies it is known that the Lower Lias is more carbonate-rich compared to the Oxford Clay and the Kimmeridge Clay, which are more clay-rich source rocks, especially the Oxford Clay. This classification can be useful in determining the source of the migrated oil. Diastrene/sterane ratio, relative abundances of C27 and C29 sterane, Sterane/hopane ratio, C29/C30 and C35/C30 hopane ratios of the seep rocks in order to classify the source as clay-rich or carbonate-rich (Table 4 and 5).



**Figure 24.** Figure showing the hopane ( $m/z$  191) distribution patterns of the samples.

	BL1	BL2	D2	D3	D4	DD	KC	MB	NC	OC	OM	ST
<b>C29 αβ/C30 αβ</b>	1.64	3.60	0.58	0.74	0.44	0.78	0.53	0.25	0.07	1.49	0.36	0.26
<b>Diasterane/ Sterane</b>	C27 βα/ ααα		0.70	1.57	1.81		1.53	0.63			0.77	0.74
	C28 βα/ ααα		9.99	8.03	4.49		0.24	1.36			1.79	8.13
	C29 βα/ ααα		4.93	9.09	1.78		0.75	1.07			1.46	0.55
<b>C35 αβ S/C30 αβ</b>			0.23	0.11	0.21			0.02			0.05	0.48
<b>C35 αβ (S+R)/C30 αβ</b>			0.36	0.16	0.30			0.05			0.08	0.62

**Table 4.** Table showin the paramaters that can be used to distinguish clay-rich from carbonate-rich source rock.

**Diasterane/sterane ratio**

Clay-rich source rocks have high diasterane vs. regular sterane content (Peters & Moldowan, 1993). Because clay minerals have a major role on transforming steroids into diasteranes. Thus, Diasterane/sterane ratio is high for clay-rich samples and low for carbonate-rich samples. From the table above this ratio ranges between 0.70 and 1.81 for C27 βα/ααα; 0.24 and 9.99 for C28 βα/ααα and 0.55 and 9.09 for C29 βα/ααα.

**C27 ααα 20R sterane and C29 ααα 20R sterane abundance**

Relative abundance of C27 ααα 20R sterane and C29 ααα 20R sterane is another parameter that can be used in determining if a source rock is clay-rich or carbonate-rich. For clay-rich source rocks C29 is greater than C27, whereas for carbonate-rich source rocks C27 is greater than C29. C27 and C29 sterane percentages are given in the Table 5. From the Table 5; C27 sterane % is higher than C29 for the samples: D2, D3 and DD while all the other samples C29 is higher than C27.

**C29 αβ/C30 αβ hopane ratio**

This ratio is high (more than 1) for carbonate-rich source rocks while low for clay-rich source rocks. From the table above the ratio is higher than 1 for the samples: BL-1, BL-2 and OC, for all the other samples it is lower than 1.

**C35 αβ S/C30 αβ hopane ratio**

C35 αβ S/C30 αβ ratio is another parameter that it is used for distinguishing clay-rich vs. carbonate rich source rocks. It is low for clay-rich and low-to-high for carbonate-rich source rocks. Table 4 shows that this ratio ranges between 0.02 and 0.48.

Based on clay- vs carbonate-rich indicators, the distinction between the Blue Lias and the Oxford Clay is not likely as the parameters of these samples are very similar to each other. It should also be noted that all these parameters can be affected by biodegradation and the deformation of the effects on these parameters increases with the increasing biodegradation.

Sterane %	ST	OM	OC	NC	MB	KC	DD	D4	D3	D2	BL-2	BL-1
<b>C27 ααα S</b>	28.40	29.54	34.56	44.63	31.23	63.13	37.33	55.81	66.63	65.04	32.67	33.45
<b>C27 ααα R</b>	31.92	33.26	33.78	29.91	28.70	23.46	50.13	22.80	64.32	44.72	25.90	31.44
<b>C27 ααα SR</b>	29.12	31.47	33.98	34.26	29.86	31.98	48.08	40.16	65.47	51.59	27.78	32.05
<b>C29 ααα S</b>	64.85	45.86	42.03	41.38	46.73	23.91	25.00	37.54	27.41	9.76	47.21	41.23
<b>C29 ααα R</b>	56.20	40.69	42.36	53.83	45.55	49.73	29.85	60.65	9.40	38.73	49.83	46.61
<b>C29 ααα SR</b>	63.08	43.18	42.27	50.15	46.09	44.19	29.07	48.49	18.37	28.94	49.10	44.99

**Table 5.** %C27 ααα Sterane and %C29 ααα Sterane.

## DISCUSSION

Basin modelling results suggest that the oil in the Wessex Basin is likely to be sourced from the Lower Lias with some contribution from the Oxford Clay. These source rocks, however, are only mature in the wells which are located to the south of the Purbeck-Isle of Wight Disturbance. The hydrocarbon generation from these source rocks started from the Early Cretaceous and peaked in the Middle Cretaceous. Other potential source rocks, the Kimmeridge Clay, the Gault Clay, the Nothe Clay and the Purbeck Shale, have not entered the oil window in any area of the basin.

The question that was next focused on was: does the oil come from the Lower Lias or from the Oxford Clay? In order to correlate the oil seeps to the source rocks, GC-MS analyses were conducted. From sterane maturity parameters all the seep samples have mature signatures, whereas all the rock samples have immature signatures. The Blue Lias and the Oxford Clay samples have values of 0.27 and 0.26 respectively. This is consistent with the basin analysis because the sampling locations are located to the north of the Purbeck-Isle of Wight Disturbance, where all the potential source rocks are possibly immature based on the basin modelling results.

Ts/Ts+Tm maturity parameter gives almost the same result, with some small difference. The differences may be due to source or oxidation, since Ts-Tm parameter is affected by all these conditions. Thus, the sterane maturity parameters are mostly honoured in this study.

C31-35 17 $\alpha$  (H), 21 $\beta$  (H) 22S and 22R homohopane distribution for the seep sample shows that the oils within the samples were deposited in similar depositional conditions.

The depositional environment correlations were done by C27-C28-C29 sterane ternary diagram. Based on the previous studies, the Lower Lias and the Oxford Clay contain type II kerogen. The ternary diagram suggests a "biodegraded oil" from type II kerogens. There are two anomalies within the diagram: ST sample and D2, D3 and DD samples. The explanation for these anomalies could be explained by the following statements:

(i) High amounts of C29 are related to terrestrial (plant) input in a sample ((Mackenzie et al., 1982; and Czochanska et al., 1988). ST sample is from the Wealden Formation which contains fluvial deposits from the Early Cretaceous. Type II organic matter might mix with the terrestrial organic mat-

ter from the Wealden deposits. This mixture might be the cause of the high concentration of the C29 for ST sample.

(ii) High amounts of C27 might be related to algae input in a sample. Since D2, D3 and DD samples are from the Lower Cretaceous Purbeck Shales and Limestone, the high concentration of C27 might be the result of the mixture of type II organic matter with lagoonal algae input, which cause these samples occur in the blues area of the ternary diagram (Figure 6.2). This mixture might also be an explanation for the relatively low maturity values.

Extracted organic matter (EOM) is also a solid parameter which may help the correlation. The values for the KC, NC, GC are very low 0.3, 0.2 and 0.15 respectively (Table 2) EOM values suggest that these rock samples have low thermal maturity which is consistent with the basin modelling results. OC and BL samples, again, have similar EOM values, meaning that the EOM values cannot be used for differentiate these two source rocks.

From the geochemical results, oil seep samples have likely the same origin based on their similarities on maturity and depositional environments. The basin modelling suggests that there are two possible source rocks within the basin: the Blue Lias and the Oxford Clay. Since these source rocks have similar type of kerogen (type II) and organic compounds and biomarker distribution, every parameter used for identification and correlation are either same or very close to each other. This makes the oil-source rock correlation based on biomarkers not feasible. However, it can still be suggested that all the oil seeps likely to have similar origin either the Blue Lias or the Oxford Clay or in some places from both of them.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

All three potential source rocks in the Wessex Basin contain II, III and II/III type kerogen with both oil- and gas-prone (Ebukanson and Kinghorn, 1985). Based on basin modelling results, among the potential source rocks within the basin, only the Lias has reached a maturity sufficient to generate and expel petroleum to charge the traps of the producing petroleum fields. The Lias is mature only in the areas where thick Wealden Group sediments were deposited, which led the underlying strata to be buried deeper (McMahon & Turner, 1998). Also,

the Lower Lias is mature in areas where it was buried deeply enough by major faulting. Basin Modelling suggests that the oil generation from the Lower Lias black shales lasted from the Early to Middle Cretaceous. The structures that were formed by this time and were not effected by the Tertiary inversion, may be the best targets for future exploration. Any structures that were formed later than this time, might also accumulate hydrocarbons, by re-migration from breached reservoirs, or by very late oil generation. The kitchen area of the Blue Lias is located in the southern part of the Purbeck-Isle of Wight Disturbance, or in the hanging walls of the Purbeck Fault and the Abbotsbury-Ridge Fault. Any possible hydrocarbon accumulations are located within these areas, due to the juxtaposition of the Lias source rock and Triassic reservoirs and the stable traps which were not affected by the Tertiary inversion.

In some areas, the Oxford Clay just reached the oil window threshold during Late Cretaceous. Some carrier beds in the basin might have charged by this source rock. However, there is no evidence to suggest if the contribution from the Oxford Clay is significant. On the other hand, the Kimmeridge Clay, the main source rock in the North Sea, is immature in the Wessex Basin, along with other potential source rocks, such as the Nothe Clay, the Gault Clay and the Purbeck Black shales due to either their low organic content or low thermal maturity.

C27-C28-C29 sterane ternary diagram suggests that the all the oil seeps might have the same origin since most of the samples are located in a small area. This is also supported with the C31-35 17 $\alpha$  (H), 21 $\beta$  (H) 22S and 22R homohopanes distribution.

Both the Basin Modelling and geochemical analyses suggest that the Blue Lias shales is likely to be the main source rock that is responsible for the oil seeps and oil accumulations with some attribution from the Oxford Clay. However, biomarker analysis is not useful to distinguish these two source rocks as they contain similar type of organic matter and similar biomarker distribution. Other potential source rocks within the basin show little or no maturity with little organic content.

### **Recommendations**

Further study could include 2D Basin Modelling in order to determine any intra-cratonic basins (localized kitchens) in which the potential source rocks might be buried enough to contribute to the

hydrocarbon accumulation within the basin. Also, as the molecular (biomarker) analysis could not distinguish the Lower Lias and the Oxford Clay it would be useful to conduct elemental or/and isotopic analyses. This way, these two source rock may be distinguished in a clear way. Another study would be the modelling the migration pathways in order to determine the alternative migration ways from the kitchen area into the carrier beds.

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### **References**

- Ainsworth, N.R., Braham, W., Gregory, F.J., Johnson, B. & King, C., 1998. The lithostratigraphy of the latest Triassic to earliest Cretaceous of the English Channel and its adjacent areas. In: Underhill, J.R. (ed) Development, Evolution and Petroleum Geology of the Wessex Basin. Geological Society, London, Special Publication 133: 103-164.
- Allen, P. A., and J. R. Underhill, 1989, Swaley cross-stratification produced by unidirectional flows, Benc1iff Grit (Upper Jurassic), Dorset, UK: J. Geol. Soc., 146, p. 241-252
- Aquino, F.; Trendel, J.; Restle, A.; Connan, J. & Albrecht, P., 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum, Advances in organic geochemistry, Wiley, chichester, 659-667.
- Arkell, W. J., 1933, The Jurassic system in Great Britain, Clarendon Press, Oxford, 681pp.
- Arkell, W. J. 1947. The geology of the country around Weymouth, Swanage, Corfe and Lulworth. Memoir Geological Survey. p. 25-58.
- Arkell, W. J., 1956. Jurassic Geology of the World . Ed. Oliver and Boyd Ltd. p. 58-123.
- Bennett, P. C., D. E. Siegel, M. J. Baedeker, and M. F. Hult, 1993, Crude oil in a shallow sand and gravel aquifer .1. hydrogeology and inorganic geochemistry: Applied Geochemistry, v. 8, p. 529-549.
- Bigge, M. A. and Farrimond, P., 1998. Biodegra-

- dation of seep oils in the Wessex Basin—a complication for correlation. In: Underhill, J. R. (ed.) *Development, Evolution and Petroleum Geology of the Wessex Basin*, Geological Society, London, Special Publications, 133, p. 373-386.
- Buchanan, J. G., 1998. The exploration history and controls on hydrocarbon prospectivity in the Wessex basins, southern England, UK. In: Underhill, J. R. (ed.) *Development, Evolution and Petroleum Geology of the Wessex Basin*, Geological Society, London, Special Publications, 133, p. 19-37.
- Butler M., Pullen C. P., 1990. Tertiary structures and hydrocarbon entrapment in the Weald Basin of southern England. In Hardman R. F. P., Brooks J. (eds) *Tectonic Events Responsible for Britain's Oil and Gas Reserves*, Geological Society, London, Special Publications, 55, pp 371–391.
- Butler, M., 1998. The geological history of the southern Wessex Basin - a review of new information from oil exploration. In: Underhill, J.R. (ed) *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publication 133: 67-86.
- Chadwick, R. A., 1986. Extension tectonics in the Wessex Basin, southern England. *Journal of the Geological Society of London*. 143, p. 465-488.
- Colter, V.S. & Harvard, D.J., 1981. The Wytch Farm Oil Field, Dorset. In: ILLING, L.V. & HOBSON, G.D. (eds) *Petroleum Geology of the Continental Shelf of North-West Europe*. Heyden, London, 494–503.
- Connan, J., 1984, Biodegradation of crude oils in reservoirs, in J. Brooks, and D. H. Welte, eds., *Advances in Petroleum Geochemistry*, v. 1: London, Academic Press, p. 299-335.
- Connan, J.; Bourouillec, J.; Dessort, D. & Albrecht, P., 1986. The microbial input in carbonate-anhydrite facies of sabkha palaeoenvironment from Guatemala, A molecular approach. In: *advances in organic geochemistry 1985. org. geochem.*, Vol. 10, 29-50.
- Cornford, C., Christie, O., Endresen, U., Jensen, P. & Myhr, M. B., 1988. Source rock and seep oil maturity in Dorset, southern England. *Org. Geochem.* 13, 399–409.
- Czochanska, Z., Gilbert, T.D., Philp, R.P., Shepard, C.M., Weston, R.J., Wood, T.A. and Woolhouse, A.D., 1988. Geochemical application of sterane and triterpane biomarkers to a description of oil from the Taranaki Basin in New Zealand, *Organic Geochemistry*, 12: 123-135.
- Ebukanson, E. J. and Kinghorn, R. R. F., 1985. Kerogen Facies in the Major Jurassic Mudrock Formations of Southern England and the Implication on the Depositional Environments of the Precursors. *Journal of Petroleum Geology*, 8. 435-462.
- Ebukanson, E. J. and Kinghorn, R. R. F., 1986a. Maturity of Organic Matter in The Jurassic of Southern England and its Relation to the Burial History of the Sediments. *Journal of Petroleum Geology*, 9, 259-280.
- Ebukanson, E. J. and Kinghorn, R. R. F., 1986b. Oil and Gas Accumulations and their Possible Source Rocks in Southern England. *Journal of Petroleum Geology*, 9, 413-428.
- Emmerton S, Muxworthy AR, Sephton MA, 2013. A magnetic solution to the Mupe Bay mystery, *Marine and Petroleum Geology*, Vol:46, Pages:165-172.
- Evans, J., Jenkins, D. & Gluyas, J., 1998. The Kimmeridge Bay oilfield: an enigma demystified. In: Underhill, J.R. (ed) *The Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publications, 133, 407-413.
- Farrimond, P., Comet, P., Eglinton, G., Evershed, R. P., Hall, M. A., Park, D. W. and Wardroper, M. K., 1984. Organic geochemical study of the Upper Kimmeridge Clay of the Dorset type area. *Marine Petroleum Geology* 1, p. 340-354.
- Hamblin, R. J. O., Crosby, A., Balson, P. S., Jones, S. M., Chadwick, R. A., Penn, I. E. and Arthur, M. J., 1992. United Kingdom offshore regional report: the geology of the English Channel. HMSO, London. p.18-38.
- Harvey, M.J. & Stewart, S.A., 1998. Influence of salt on the structural evolution of the Channel Basin. In: Underhill, J.R. (ed) *The Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publications, 133, 241-266.
- Hawkes, P.W., Fraser, A.J. & Einchcomb, C.C.G., 1998. The tectono-stratigraphic development and exploration history of the Weald and Wessex basins, Southern England, UK. In: Underhill, J.R. (ed) *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publications, 133, 241-266.

- tion and Petroleum Geology of the Wessex Basin. Geological Society, London, Special Publication 133: 407-413.
- Huang, W., and W. G. Meinschein., 1979, Sterols as ecological indicators: *Goechimica et Cosmochimica Acta*, v. 43, p. 739-745, doi:10.1016/0016-7037(79)90257-6.
- Hunt, J., (1996). *Petroleum geochemistry and geology*, 2nd ed., Freeman and Company, New York, 743.
- James G.B., 1998 *The exploration history and controls on hydrocarbon prospectivity in the Wessex Basin, Southern England*, UK: Geological Society, London, Special Publications, V 133 p. 19-37.
- Karner, G. D., Lake, S. D. & Dewey, J. F., 1987. The thermal and mechanical development of the Wessex Basin, southern England. In: Coward, M. P., Dewey, J. F. & Hancock, P. L. (eds) *Continental Extension Tectonics*. Geological Society, London, Special Publications, 28, 517-537.
- Lake, S. D. & Karner, G. D., 1987. The structure and evolution of the Wessex Basin, southern England: an example of inversion tectonics. *Tectonophysics*, 137, 347-378.
- Law, A. 1998. Regional uplift in the English Channel: quantification using sonic velocity. In: Underhill, J.R. (ed) *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publication 133: 187-197.
- Lees, G.M. and Cox, P.T., 1937. The geological basis for the search for oil in Great Britain by the D'Arcy Exploration Co. Ltd. *Quarterly Journal of the Geological Society*, London, 93, 156-190. Oil in the Bencliff Grit. Oil Seep at Bran Point.
- Mackenzie, A.S., Lamb, N.A. and Maxwell, J.R., 1982. Steroid hydrocarbons and the thermal history of sediments, *Nature*, 295: 223-226.
- Mcmahon, N. A. & Turner, J. D., 1998. The documentation of a latest Jurassic-earliest Cretaceous uplift throughout southern England and adjacent offshore. In: Underhill, J.R. (ed) *The Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publications, 217-240.
- Melville, R. V. and Freshney, E. C., 1982. *The Hampshire Basin and adjoining areas*, Fourth Edition, British Regional Geology Series, Institute of Geological Sciences, Natural Environment Research Council, London, HMSO.
- Miles, J. A., Downes, C. J. and Cook, S. E., 1993. The fossil oil seep in Mupe Bay, Dorset: a myth investigated. *Marine and Petroleum Geology*, 10, p. 58-70.
- Ourisson, G., Albrecht, P. and Rohmer, M., 1979. The hopanoids. *Paleochemistry and biochemistry of a group of natural products*, *Pure Applied Chemistry*, 5: 709-729.
- Ourisson, G., Albrecht, P. and Rohmer, M., 1984. The microbial origin of fossil fuels, *Sci. Am.*, 251: 44-51.
- Parfitt M., Farrimond P., 1998. The Mupe Bay oil seep: a detailed organic geochemical study of a controversial outcrop. In: Underhill J. R. (ed.) *Development, Evolution and Petroleum Geology of the Wessex Basin*. Geological Society, London, Special Publications, 133, 387-398.
- Penn, I. E., R. A. Chadwick, S. Holloway, G. Roberts, T. C. Pharaoh, J. M. Allsop, A. G. Hulbert, and I. M. Bums., 1987. Principal features of the hydrocarbon prospectivity of the Wessex-Channel Basin, UK, in J. Brooks and K. Glennie, eds, *Petroleum Geology of North West Europe*, p. 109-118.
- Peters, K.E. & Moldowan, J.M., 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. In: *Organic Geochemistry* vol. 17 pp. 47-61.
- Scott, J. & Colter, V.S., 1987. Geological aspects of current onshore Great Britain exploration plays. In: Brooks, J. & Glennie, K. (eds), *Petroleum Geology of North West Europe*, Graham & Trotman, London, 95-107.
- Scotchman I. C., 1994. Maturity and burial history of the Kimmeridge Clay Formation, onshore UK: a biomarker study. *First Break*, 12, 193-202.
- Selley, R. C., and R. Stoneley., 1984, *A field guide to the petroleum geology of the Wessex basin*, Petroleum Exploration Society of Great Britain field trip.
- Selley, R.C., Stoneley, R., 1987. Petroleum habitat in south Dorset. In: Brooks, J., Glennie, K.W. (Eds.), *Petroleum Geology of North West Europe*. Graham and Trotman, London, pp. 139-148.
- Selley, R. C., 1992. Petroleum seepages and im-

- pregnations in Great Britain. *Marine and Petroleum Geology*, 9, 226–244.
- Shanmugam, G., 1985, Significance of coniferous rain forests and related organic matter in generating commercial quantities of oil, Gippsland Basin, Australia: AAPG Bulletin, v. 69, p. 1241–1254.
- Stoneley, R., 1982. The Structural Development of the Wessex Basin. *Journal of the Geological Society*, London. 139. 543-554.
- Stoneley, R. and Selley, R.C., 1991. A Field Guide to the Petroleum Geology of the Wessex Basin (3rd edition). R. C. Selley & Co., Dorking.
- Strahan, A., 1920, Special reports on the mineral resources of Great Britain, v. VII, Mineral Oil, Mem. Geol. Surv., 124pp.
- Underhill, J.R. & Paterson, S., 1998. Genesis of tectonic inversion structures: seismic evidence for the development of key structures along the Purbeck-Isle of Wight Disturbance. *Journal of the Geological Society*, London 155: 975-992.
- Underhill, J.R. & Stoneley, R., 1998. Introduction to the development, evolution and petroleum geology of the Wessex Basin. In: Underhill, J.R. (ed) Development, Evolution and Petroleum Geology of the Wessex Basin. Geological Society, London, Special Publication 133: 1-18.
- Van Graas, G., 1990. Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold, *Organic Geochemistry*, Vol. 16, 1025-1032.
- Watson, D. F., Hinde, A. D. & Farrimond, D., 2000. Organic geochemistry of petroleum seepages within the Jurassic Benclyff grit, Osington Mills, Dorset, UK. *Petroleum Geoscience*, 6, 289–297, doi: 10.1144/petgeo.6.4.289.
- West, Ian M., 2013. Kimmeridge region, Dorset; Geology of the Wessex of southern England. Internet site. <http://www.southampton.ac.uk/~imw/index.htm#List-of-Webpages>. Ian M. West, Romsey, Hampshire.
- Wimbledon, W. A., P. Allen and A. 1. Fleet., 1996, Penecontemporaneous oil-seep in the Wealden (early Cretaceous) at Mupe Bay, Dorset, U.K. *Sed. Geol.*, v. 102, p. 213-220.
- Ziegler, P.A., 1990. Geological Atlas of Western and Central Europe. Shell Internationale Petroleum Maatschappij B.V., 2nd Ed., pp. 239.

## Appendix

### Appendix 1: Peaks identification for hopanes and sterane distributions

#### Hopanes (*m/z* 191 mass chromatogram)

Ts 18 $\alpha$  (H)-22, 29, 30- Trisnorneohopane

Tm 17 $\alpha$  (H)-22, 29, 30- Trisnorhopane

C<sub>29</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane

C<sub>29</sub> - 17 $\beta$  (H), 21 $\alpha$  (H) – Hopane

C<sub>30</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane

C<sub>31</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22S)

C<sub>31</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22R)

C<sub>31</sub> - 17 $\beta$  (H), 21 $\alpha$  (H) – Hopane (22S) – Moretane

C<sub>32</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22S)

C<sub>32</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22R)

C<sub>32</sub> - 17 $\beta$  (H), 21 $\alpha$  (H) – Hopane (22S) – Moretane

C<sub>33</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22S)

C<sub>33</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22R)

C<sub>34</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22S)

C<sub>34</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22R)

C<sub>35</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22S)

C<sub>35</sub> - 17 $\alpha$  (H), 21 $\beta$  (H) – Hopane (22R)

C<sub>30</sub> – C<sub>35</sub> – Hopene

C<sub>32</sub> – C<sub>35</sub> – Benzopene

C<sub>19</sub>-20-21-23-24-25-26-27 Tricyclic Terpene

#### Steranes (*m/z* 217 mass chromatogram)

C27 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20S)

C27 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20R)

C27 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20S)

C27 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20R)

C28 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20S)

C28 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20R)

C28 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20S)

C28 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20R)

C29 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20S)

C29 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20R)

C29 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20S)

C29 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20R)

C30 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20S)

C30 5 $\alpha$  (H), 14 $\alpha$  (H), 13 $\beta$  (H) sterane (20R)

C30 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20S)

C30 5 $\alpha$  (H), 14 $\beta$  (H), 13 $\beta$  (H) sterane (20R)

#### **Diasterane**

C21 13 $\alpha$  (H), 17 $\alpha$  (H) –Diasterane (22S)

C21 13 $\alpha$  (H), 17 $\alpha$  (H) –Diasterane (22R)

C21 13 $\alpha$  (H), 17 $\beta$  (H) –Diasterane (22S)

C21 13 $\alpha$  (H), 17 $\beta$  (H) –Diasterane (22R)

*Provenance And Migration Of The Petroleum Fluids In The Wessex Basin, Southern England*

C22 13 $\alpha$ (H), 17a (H) –Diasterane (22S)	C28 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20S)
C22 13 $\alpha$ (H), 17a (H) –Diasterane (22R)	C28 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20R)
C22 13 $\alpha$ (H), 17 $\beta$ (H) –Diasterane (22S)	C28 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20S)
C22 13 $\alpha$ (H), 17 $\beta$ (H) –Diasterane (22R)	C28 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20R)
C27 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20S)	C29 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20S)
C27 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20R)	C29 13 $\beta$ (H), 17 $\alpha$ (H) diasterane (20R)
C27 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20S)	C29 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20S)
C27 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20R)	C29 13 $\alpha$ (H), 17 $\beta$ (H) diasterane (20S)