



## CHEMICAL ANALYSIS OF NORTH SEA OIL AND KIMMERIDGE IMMATURE SOURCE ROCK

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### ABSTRACT

Thin layer chromatography, open column chromatography and soxhlet extraction were the three separation techniques used to fractionate the aliphatic and aromatic hydrocarbons from North Sea oil and Kimmeridge immature source rock. Gas chromatography was used to analyse the n- alkanes, pristane and phytane. The pristane and phytane ratio of the two different samples (North Sea oil and Kimmeridge immature source rock) were found to be 1.5 and 0.79 respectively. Values less than one indicate anoxic setting and greater than 1 indicates oxic setting. Carbon preference index (CPI) was also calculated to know the maturity of the North Sea oil. The Pr/Ph of the North Sea oil and Kimmeridge source rock show that North Sea oil was deposited in Oxic environment while Kimmeridge source rock was deposited under anoxic environment. The CPI value of the oil indicates maturity and non biodegraded oil.

**Keywords:** Anoxic, Carbon preference index, Immature source rock, North Sea oil, Oxic, Pr/Ph.

### INTRODUCTION

North Sea oil is a mixture of hydrocarbons comprising liquid and natural gas, produced from oil reserves beneath the North Sea. In the oil industry, the term North Sea often includes areas such as the Norwegian Sea and the area known as “West of Shetland”. North Sea is one of the world’s most important oil and gas provinces which were dominated by upper Jurassic marine Kimmeridge source rock that is believed to be formed under anoxic setting (Karlsen, 2004; Paul, 1986). In petroleum geology, source rock refers to rocks from which hydrocarbons have been generated (Matthews, 2008). They form one of the necessary elements of a working petroleum system. Kimmeridge clay is considered a major oil source rock for the North Sea hydrocarbon province. However, geochemically, onshore basin margin sediments contain rich potential source horizons with mainly type I and type II oil prone kerogen, but are immature. Some deeper Cleveland Basin sediments have reached marginal maturity. Burial history reconstruction suggests significant formation palaeoburial depths in central areas of Cleveland and Wessex Basins (Paul, 1986). Kimmeridge Source rock was deposited in the Wessex Basin (Dorset, England) during the late Jurassic times and is mainly composed of argillaceous sediments (Miller, 1990; Paul Farrimond., 1984; Gallois., 2000; Paul, 1986). It has been reconstructed that sedimentation occurred in a quit shallow (50-100m average water depth) marine environment with maximum depth of 200-

500m in the grabens. It has been widely postulated that Wessex basin was periodically anoxic (Paul, 1984).

Crude oil and Source rocks contain complex mixture of different compounds that can be separated using different methods. The commonly used methods for separation of different compounds from a complex mixture such as crude oil or source rocks are open column liquid chromatography and thin layer Chromatography (TLC). In these procedures, two different methods were employed to fractionate the Saturates (aliphatic hydrocarbons), aromatics, nitrogen, sulphur and oxygen (NSO’s). The aim of this work is to fractionate different organic compounds from North Sea oil and Kimmeridge immature source rock using open column liquid chromatography and thin layer chromatography respectively and also to identify individual components (n-alkanes, pristane and phytane) by other analytical method (Gas chromatography). The pristane and phytane ratio and carbon preference index were also calculated in order to know the depositional environment and maturity level of the North Sea oil.

### Materials and Methods

**Materials:** Weighing balance, Rotary evaporator, Small glass column, Streams of Nitrogen, Gas chromatography Machine (GC), Petroleum ether, Dichloromethane (DCM), Silica, Alumina, Soxhlet extractor, Tema mill, Retort stand, Nitrogen stream evaporator, Rhodamine G6, UV Machine, North Sea Oil and Kimmeridge Source rock. The North

Sea oil sample was collected in the vials from the North Sea oil field in Norway while Kimmeridge immature source rock sample was collected from the outcrop of the Wessex basin in Dorset, southern England by the use of hammer.

## Methods

**A. Fractionation:** Open Column liquid chromatography was used in this project to separate different fractions from North Sea Oil. The Column is made up of glass tube with stopcock at one end and solvent reservoir at other end. The length and diameter for the column are typically 50-100cm and 10-20mm respectively. The Column was prepared by first adding a piece of extracted cotton down to the narrower part of the glass tube. A quantity of 70ml of Petroleum ether (low polarity solvent) was poured into the glass tube and followed by Silica slurry (silica and petroleum ether) and then Alumina slurry (alumina and petroleum ether), but the Polytetrafluoroethylene valve (PTFE) was tied during the column preparation to prevent leaking of the solvents. Some amount of Alumina was added into a weighed and clean vial. The weight of vial and alumina was recorded to be 8526.7mg. Three drops of oil sample was also added onto alumina in a weighed clean vial and then mixed together, the overall weight of the vial was found to be 8602mg, and therefore the weight of oil sample used in the experiment was calculated to be 75.3mg. The mixture of Oil sample and alumina in the vial was carefully poured into the glass column. Seventy millilitre (70ml) of Petroleum ether was measured and poured gradually into the solvent reservoir to elute the saturates (aliphatic hydrocarbon) from the oil sample. The Saturate was collected in a clean weighed round bottom flask.

Another 70ml of dichloromethane (more polar solvent) was also measured and poured gradually into the column to elute aromatic hydrocarbon in separate clean weighed round bottom flask. Aliphatic hydrocarbon fraction collected in a weighed round bottom flask was taken to the rotary evaporator to evaporate the excess solvent. The round bottom flask and evaporated saturate was re-weighed again to obtain the weight of extract and round bottom flask. Few drops of dichloromethane (DCM) were used to retrieve the evaporated extract, which was then transferred into a clean weighed vial by the aid of pipette. The vial and washed extract were also evaporated under a stream of nitrogen. The weights of empty clean vial and vial with evaporated saturate were recorded as 3215.5mg and 3233.4mg respectively, and the weight of saturate was

calculated to be 17.9mg. The aliphatic fraction was then taken to GC machine for analysis and

the GC trace for the fraction obtained was shown in Fig. 1. (Paul, 1984).

## B. Extraction of Source Rock.

The rock sample was cleaned by washing using Petroleum ether, and then crushed into powder using clean disc (Tema mill) a mechanical device. 100g of powdered rock sample was weighed and used to extract the extractable organic matter from the source rock. During the extraction, 70ml mixture of dichloromethane (DCM) and Petroleum ether in the ratio of 93:7 respectively was prepared into a 100ml beaker, some copper chips and anti bumping granules were added into the beaker in order to remove sulphur by forming copper sulphate (CuS) and reduce bumping during extraction respectively. The powdered rock sample was transferred into thimble and extracted using soxhlet extractor. After extracting the extractable organic matter, the extract was transferred into a weighed clean round bottom flask using a pipette and then taken to rotary evaporator to remove the excess solvents. The round bottom flask and the evaporated extract were re-weighed and the weight of the extract was recorded as 93mg (Paul, 1984).

## C. Thin layer chromatography separation (TLC).

Thin layer chromatography (TLC) was used in this work to fractionate the aliphatic and aromatic fractions from the source rock extract. A thin layer plate was prepared using aqueous slurry of 0.5mm thick keiselgel 60G. A partition line of about 2cm was drawn from the edge of the coated plate to separate the standard and the sample extract. The sample extract was used to make dots on the silica coated plate using a clean pipette at a distance of about 1cm apart, the pipette was used again to fill in the gaps between the oil light at the partition angle. Another standard oil was used to make few dots beside the partition line on the plate. Petroleum ether (200ml) was poured in to the tank, and the dotted side of the plate was dipped in to the tank and left until the solvent reached the height of the plate (about 1cm to the edge). The plate was removed from the tank and allowed to dryness. The dried plate was sprayed with a dye called Rhodamine G6 and viewed under UV light where two distinct regions for light hydrocarbon (aliphatic hydrocarbon) and heavy hydrocarbon (aromatic and NSO) were marked. The two distinct regions for light and heavy hydrocarbons were scraped in separate places. Two small columns were used to wash the aliphatic and aromatic fractions respectively (Paul, 1984).

#### D. Preparation of small column

Two small glass tubes were tied at different retort stand as in open column liquid chromatography, and the extracted cotton was placed at the base of each column followed by DCM and alumina slurry. The scraped corresponding band containing the light fraction and heavy fraction were poured in to two different small columns followed by 70ml mixture of dichloromethane (DCM) and petroleum ether in the ratio of 50:50 for aliphatic fraction and aromatic fraction respectively. The two different fractions were collected in two separate round bottom flasks which were then taken to rotary evaporator to remove the excess solvent. Few drops of DCM was used to retrieve the fractions and then transferred in to weighed clean vials by the use of pipette. The vials and washed fractions were re-evaporated under stream of nitrogen and also re-weighed to obtain the weight of the fractions. The weights of

aliphatic and aromatic were found to be 10.5mg and 9.1mg respectively. The two fractions were taken to GC machine for analysis and the GC trace shown in Fig. 2 was obtained (Paul, 1984).

#### Results and Discussion

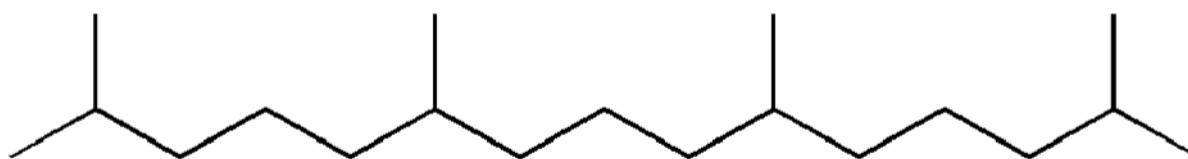
##### Pristane/Phytane ratio

Pristane and Phytane ratio for North Sea oil is calculated below; using the measured height of pristane and phytane peaks after the carbon 17 and 18 respectively from the GC trace in Fig. 1.

$$\frac{Pr}{Ph} = \frac{4.7}{3.1} = 1.5$$

For Kimmeridge immature source rock, the pristane and phytane peaks after carbon 17 and 18 in the GC trace were also measured using a ruler, and their values are used below to calculate their ratio.

$$\frac{Pr}{Ph} = \frac{8.8}{11.2} = 0.79$$



Chemical structure of Pristane



Chemical structure of Phytane

The Pristane and Phytane ratio for Column separation of North Sea oil is 1.52 and that for TLC of Immature source rock is 0.79. Both Pristane and Phytane are believed to be derived from phytol (a side chain of chlorophyll) which undergoes different chemical reaction (diagenesis) in water column to form pristane and phytane. Early studies of the diagenetic fate of phytol suggested that different products are formed under different redox conditions (Killops, 2005). Under oxidizing conditions, a significant proportion of phytol, a C<sub>20</sub> compound can be oxidized to phytanic acid which may undergo decarboxylation to pristane, a C<sub>19</sub> compound and finally reduced to pristane. However, under anoxic conditions phytol is more likely to undergo reduction and dehydration to phytane through dihydrophytol (phytanol) or phytene, with the preservation of all 20 carbon atoms in the product (Killops, 2005). On this basis,

it was suggested that pristane-phytane ratio may provide a measure of redox conditions during diagenesis with values <1 being anoxic conditions and values >1 suggesting oxicity. Based on this, the pristane-phytane ratio obtained from column separation of North Sea oil, which is 1.52 (>1) indicates oxic condition during diagenesis of the North Sea oil, while for immature source rock, the Pristane-Phytane ratio obtained from TLC is 0.79 (<1) and therefore indicates anoxic condition during diagenesis of the source rock. However, the depositional environment of the North Sea oil is anoxic, but in this work, the Pr/Ph obtained (1.5) indicates oxicity; this is due to the fact that the oil sample used (North Sea oil) in this work was collected and kept for a long period of time and therefore changed its redox condition.

**Carbon Preference Index (CPI)**

Carbon Preference Index (CPI) is defined as the average sum of the ratio of odd numbers for n-alkanes to the sum of even numbers for n-alkanes.

CPI is used to determine the maturity of oil or source rocks

$$CPI = \frac{1}{2} \left[ \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right]$$

CPI for GC trace in North Sea oil.

$$CPI = \frac{1}{2} \left[ \frac{3.8 + 2.2 + 1.1 + 0.4 + 0}{4.3 + 3.1 + 1.7 + 0.6 + 0.1} + \frac{3.8 + 2.2 + 1.1 + 0.4 + 0}{3.1 + 1.7 + 0.6 + 0.1 + 0} \right]$$

$$CPI = \frac{1}{2} \left[ \frac{7.5}{9.8} + \frac{7.5}{5.5} \right] = 1.06$$

The n-alkane distribution of the North Sea oil was found to have the CPI value of 1.06. According to (Bray E.E., 1961, REQUEJO, 1994) the CPI value of recent sediments ranged from 2.4 to 5.5 while that of the ancient sediment ranged from 0.95 to 2.4. Therefore, based on this classification, the North Sea oil was found to be much matured considering its CPI value of 1.06 which indicates the oil has almost equal distribution of molecules containing even and odd number of atoms. Quite number of works has been carried out on Kimmeridge source rocks obtained from Wessex Basin in Dorset (Southern England) to understand the depositional condition/environment of the sediments. The work could either be on the matured or immature sediments/source rocks. (Paul Farrimond, 1984) carried out geochemical investigation of rock samples taken from upper Kimmeridge Clay near Dorset England, and the investigation shows that the samples contain immature source rock of marine origin. However, the results of other

samples are in agreement with paleoenvironmental model proposed by (Tyson, 1979) for deposition of Kimmeridge Clay, where the different lithologies are controlled by a fluctuating oxic/anoxic boundary with only the organic-poor mudstones being deposited in relatively oxygenated waters

**Conclusion**

The pristine-phytane ratio of the North Sea oil and Kimmeridge Source rock indicated oxic and anoxic setting respectively during their deposition. However, North Sea oil was said to be deposited in an anoxic setting, but due to over maturing of the oil, it's pristine-phytane ratio indicates oxic setting during its deposition. Similarly, carbon preference index (CPI) value obtained showed that the oil is matured with almost equal distribution of molecules containing even and odd number of atoms. Therefore, the oil is free from biodegradation; hence contain all the mixtures of crude oil.

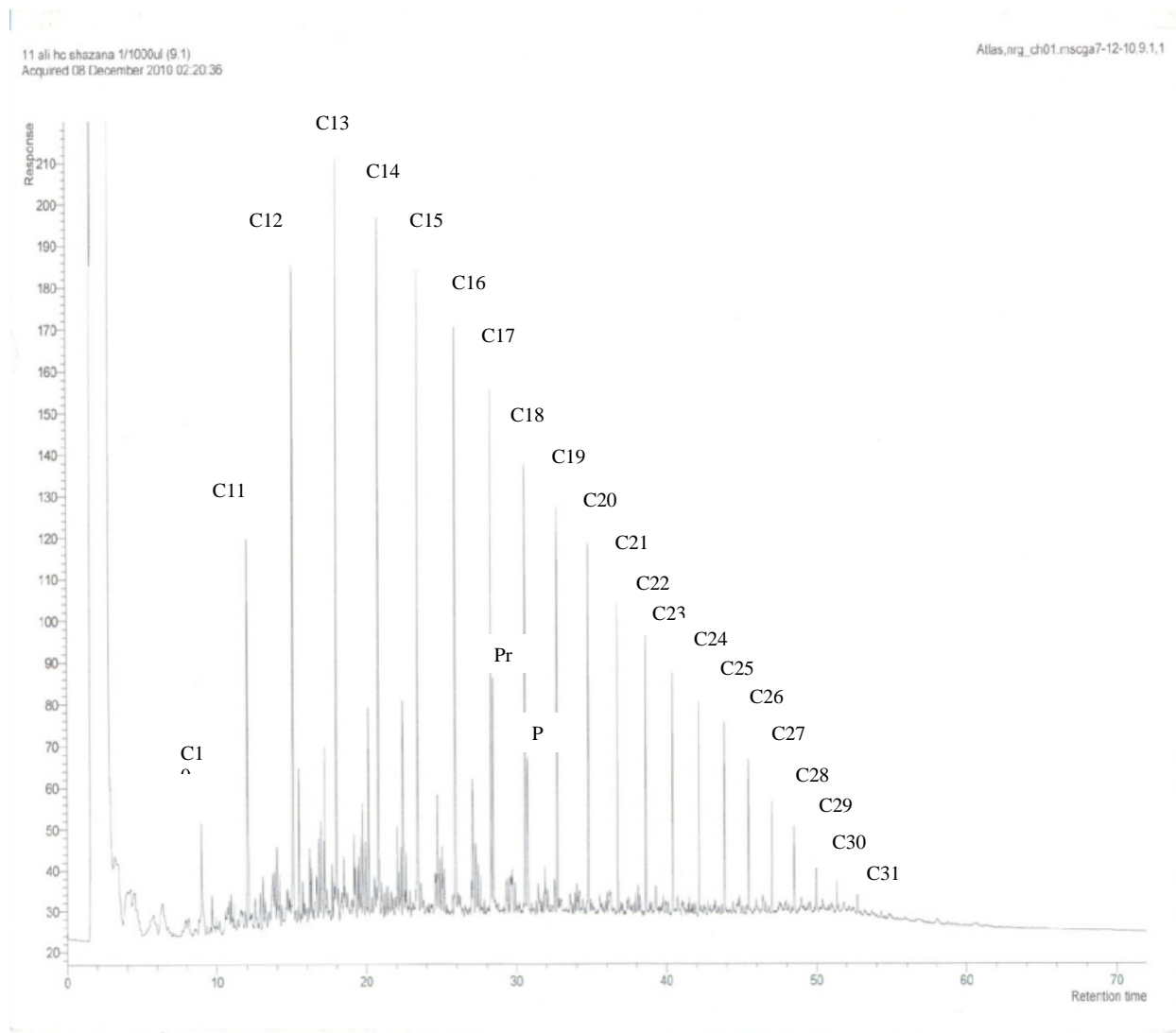


Fig 1 Aliphatic Hydrocarbon GC trace of North Sea Oil

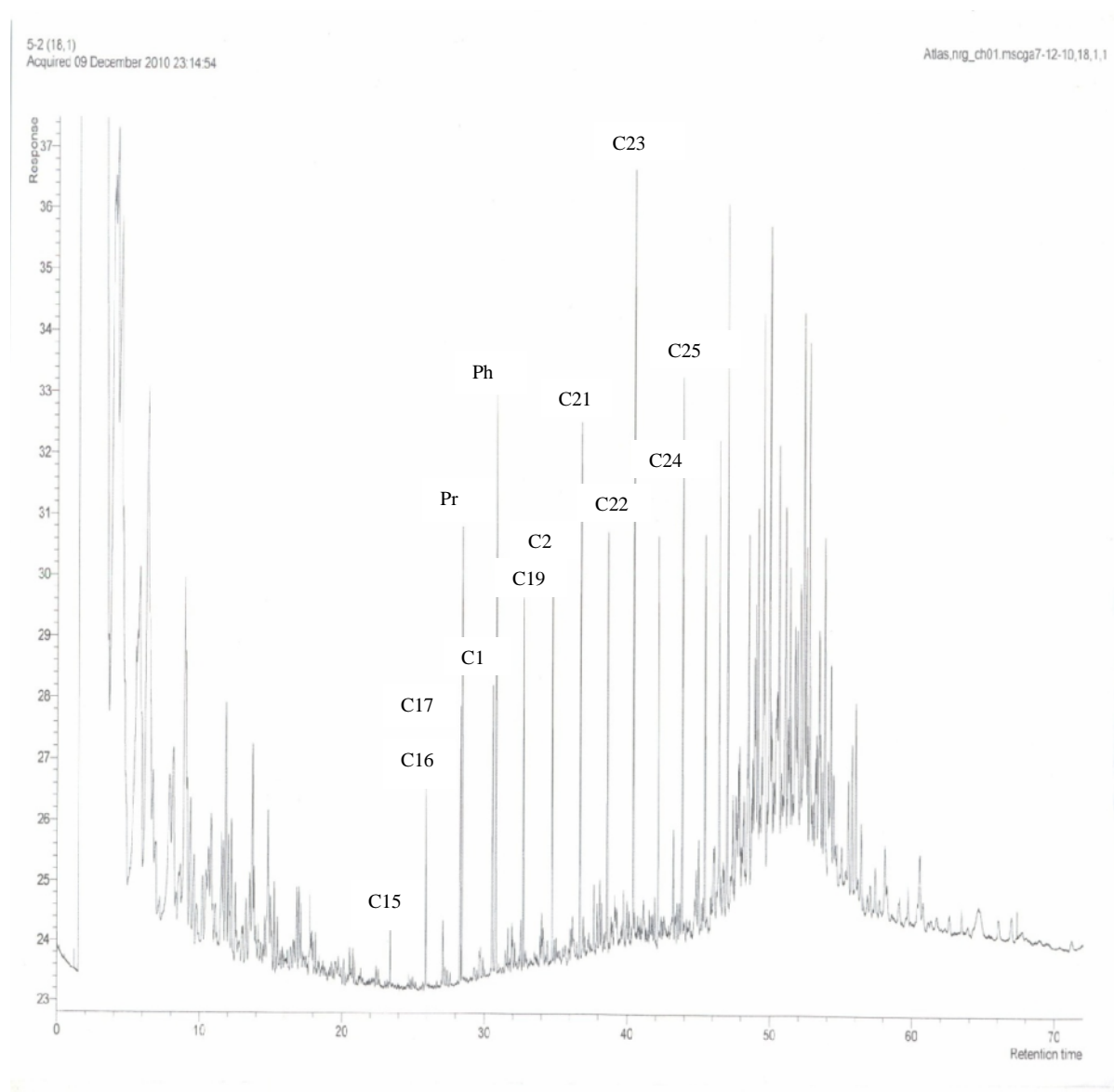


Fig. 2 Aromatic GC trace of Kimmeridge immature source rock

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