



Geochemical Characterization Of Organic Matter Using Steam Pyrolysis Experiments On Mid-Cretaceous Oil Shale In The Anambra Basin, Southeast Nigeria

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ABSTRACT

Steam pyrolysis experiments were performed on immature oil shale samples from Lopkanta in the Nkporo Shale, Anambra Basin, Nigeria, using a maximum temperature of 350 °C with up to 98 h exposure time at that temperature. The objectives were to study geochemical and petrographical changes in the source material during stepwise increase in maturity, in steam conditions, comparing the properties of expelled oil with the bitumen retained in the solid residue after experimentation. Petrographical and geochemical parameters such as vitrinite reflectance and Tmax, indicated an increase in maturity related to the exposure time of the organic matter to the maximum temperature. However, biomarker ratios such as 22S/(22S + 22R) C₃₁ and C₃₂ homohopanes, 20S/(20S + 20R) and $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ C₂₉ sterane, which are considered to be indicators of organic matter maturity levels, did not reach their equilibrium values. Some biomarkers frequently used as indicators of specific sources and/or paleoenvironments of deposition such as hopane/sterane ratio, and the concentrations of C₂₇ and C₂₉ steranes showed significant variations related to the stage of maturity. Based on the evaluation of Rock-Eval parameters, the transformation ratios in steam pyrolysis conditions reached levels higher than 80% in samples having 9 and more hours of exposure time to maximum temperature. Bitumen was found to be enriched in components of heavier molecular weight (resins and asphaltenes), whereas the expelled oils contained higher quantities of aliphatic and aromatic components. At relatively low maturity levels the n-alkane distribution of expelled oils indicate a somewhat higher maturity level when compared to the n-alkane distribution of the bitumen retained in the source rock, whereas at higher maturity levels the n-alkane distribution for the expelled oil and for the bitumen is very similar.

Keywords: Bitumen, Expelled oil, Steam pyrolysis, Lokpanta Oil Shale, Anambra Basin.

INTRODUCTION

The area of study is located between latitudes 5°55'N and 6°30'N and longitudes of 7°15'E and 7°40'E within the Anambra Basin (Fig. 1). The Anambra Basin is a big intra-continental basin that forms an arm of the lower Benue Trough (Obaje et al., 2004) with its NE-SW trending towards the Niger Delta (Fig. 1). Petroleum exploration in the Anambra basin was triggered by the occurrence of surface seeps and dates back to the early 1930s (Kulke, 1995). However, due to the Santonian inversion and the predominance of terrestrial sediments, as well as discoveries in the prolific Niger Delta in the south Ekweozor and Gormly (1983), the petroleum potential of this area has been under exploration and exploitation.

Pyrolysis is a technique that can be defined as the thermal decomposition of organic matter through the application of heat in the absence of oxygen. Pyrolysis experiments can be carried out with or without the presence of liquid water as well as in the presence of water steam. In the petroleum industry, pyrolysis is employed to simulate oil generation during the subsidence of a basin, carrying simulations in the absence (anhydrous pyrolysis) and in the presence (hydrous pyrolysis) of liquid water during the heating process.

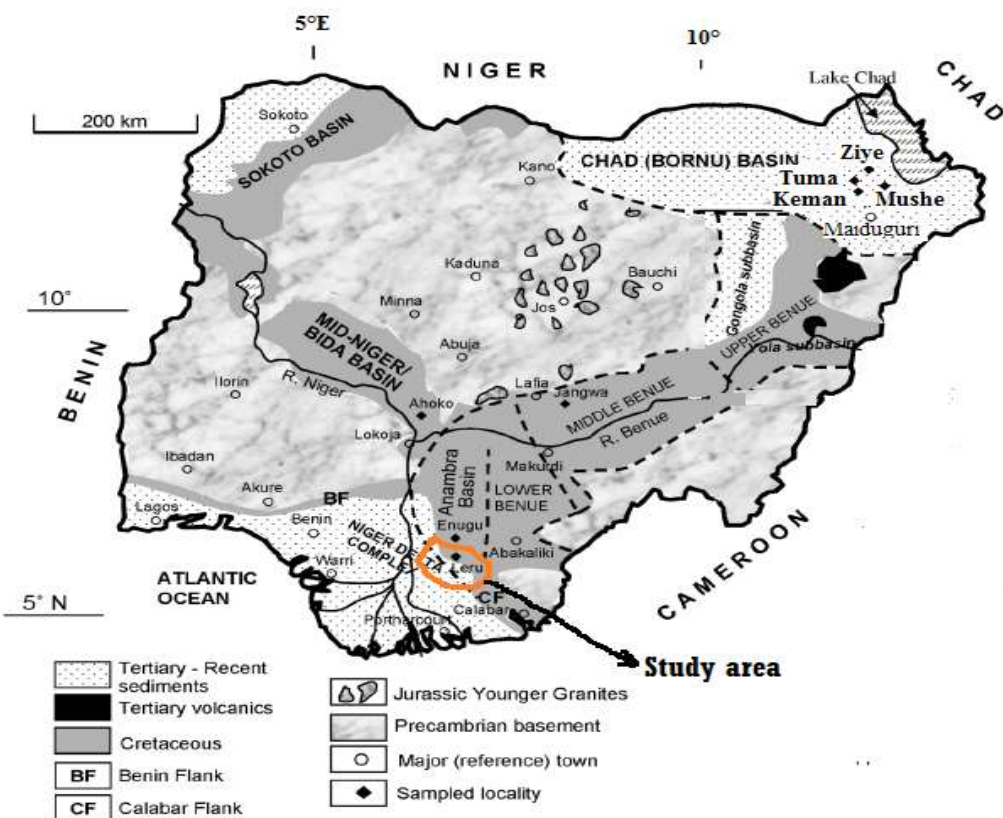


Fig. 1: Geological map of Nigeria showing the study location in the Lower Benue Trough (modified from Obaje et al., 2011).

The products of these two types of pyrolysis provide a better understanding of the mechanisms taking place in natural systems during the process of oil generation and have been widely studied by a number of authors (Comet et al., 1986; Eglinton and Douglas, 1988; Koopmans et al., 1998; Lewan, 1993; Lewan et al., 1986; Lewan et al., 2006). On the other hand, pyrolysis experiments in the presence of water steam, known as steam pyrolysis, are frequently used in the petroleum industry aiming the recovery of heavy oils due to the fact that water steam at high temperatures changes the physical properties of these types of oil, mainly by decreasing their viscosities (Hongfu et al., 2002; Liu and Fan, 2002). Another use for steam pyrolysis is the extraction of solid fuels, being reported a significant yield increase and variation in liquid products composition when compared with other extraction techniques (Minkova et al., 1991; Razvigorova et al., 1995; Franco et al., 2010). However, not much has been done on possible variations in geochemical and petrographic parameters in rocks submitted to steam pyrolysis as well as biomarkers ratios in the liquid products generated.

This study aimed to reveal the influence of water steam on the maturation parameters like Tmax and vitrinite reflectance on mid-Cretaceous Lokpanta oil shale in the Nkporo Shale, as well as the principal biomarker ratios for the generated liquid hydrocarbons.

Regional Geological Setting

The tectonism in Southern Nigeria probably started in Early Cretaceous, with the separation of Africa from South America due to the opening of the Atlantic. This resulted in the development of the Benue Trough which stretched in a NE-SW direction (Fig. 1), resting unconformably upon the Pre-Cambrian basement complex. It extends from the Gulf of Guinea to the Chad Basin and is thought to have been

formed by the Y-shaped (RRR) triple junction ridge system that initiated the breaking up and dispersion of the Afro-Brazilian plates in Early Cretaceous (Kogbe, 1989).

After the evolution of the Benue Trough, sediments started depositing in the Trough. Stages of sedimentations in the trough were in three cycles; the Pre-Cenomanian deposit of Asu River Group followed by the Cenomanian-Santonian sedimentation. According to Hogue (1977) the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both Afikpo Syncline and Anambra basin, represented the third cycle of sedimentation which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone. The Nkporo group is overlain conformably by the Coal Group consisting of the Mamu, Ajali and Nsukka Formations that form the terminal units of the Cretaceous series.

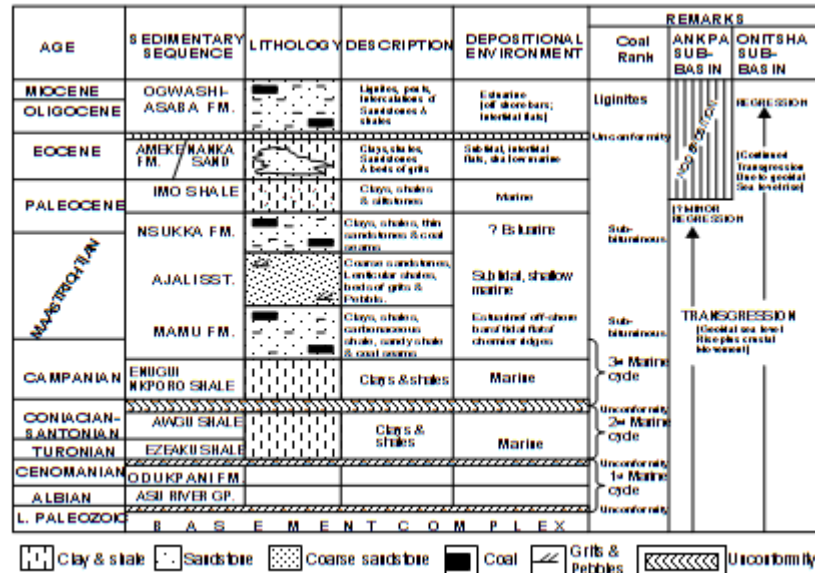


Fig. 2: The stratigraphy of the Anambra Basin southeastern Nigeria (Modified Uzoegbu et al., 2015).

Stratigraphic Setting

The sandstones which is about 330 m thick is an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200 m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reyment, 1965; Nwajide, 1990) (Fig. 2). The Ajali Formation is typically characterized by white coloured sandstone (Reyment, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey - blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

MATERIALS AND METHODS

Analytical preparation

The sample used in this study was from the mid-Cretaceous Nkporo Shale of the Lokpanta oil shale, Anambra Basin, Nigeria. Ehinola et al. (2005) examined the geologic mapping and Rock Eval characteristics of 17 samples of the Lokpanta oil shale recovered from drilling/coring. The studied drill-core samples are taken from sites located near the towns of Lokpanta, Onoli-Awgu and Acha (Fig. 1). The oil shale containing organic-rich rocks of type I/II kerogen is considered to have the greatest oil generation potential of the basin (Ekweozor and Gormly, 1983; Obaje et al., 2004; Franco et al., 2010; Uzoegbu, 2010; Uzoegbu et al., 2014; Akaegbobi et al., 2017). The oil shale was collected from a drill-

core at Lokpanta, Abia-Imo States. The sample was subsequently crushed, homogenized, and the 0.1–0.2 cm size fraction was retained for steam pyrolysis experiments.

Steam pyrolysis experiments

Steam pyrolysis experiments were performed in a stainless steel reactor (Parr Instrument Company, model 4651, 500 ml) connected to a Parr temperature controller Model 4842. Fifty grams of crushed sample and 50 ml of distilled water were put in the Stainless Steel reactor, which was purged with nitrogen prior to the pyrolysis experiment in order to remove the air. To determine the compositional variations in the bitumen and expelled oil, 6 experiments were carried out at the same pressure and temperature condition, 2100 psi and 350 °C, respectively. The exposure time to the maximum temperature varied between 0 (immediate heating shutoff) and 98 h. The heating rate was 3.7 °C/min and the temperature was continuously monitored and kept within ± 1 °C of the setting point.

Extraction from liquid chromatography

Liquid products were separated after cooling. Expelled oil was separated from water in a separation funnel and the autoclave was rinsed with dichloromethane order to remove traces of expelled oil. The bitumen generated under steam pyrolysis conditions was extracted from the pyrolyzate sample by Soxhlet extraction with dichloromethane for 48 h. After extraction, the bitumen was transferred to a rotary vacuum evaporator for solvent removal.

Saturate, aromatic and NSO (resins and asphaltenes) fractions from both bitumen and expelled oil were separated in a Medium Pressure Liquid Chromatograph (MPLC), equipped with a HPLC pump and SiO₂ column. The solvents used for separation of the fractions were n-hexane for the aliphatic fraction, n-hexane/toluene (60/40) for the aromatic fraction, and toluene/methanol (60/40) for the heterocomponents (NSO).

TOC and Rock-Eval pyrolysis

Total organic carbon (TOC) and Rock-Eval pyrolysis were carried out on the original sample (unheated) and on the solid residues obtained from the steam pyrolysis experiments. TOC analyses were performed in a carbon and sulfur non-dispersive analyzer SC-444, Leco_ equipped with an infrared detector and Rock-Eval pyrolysis analyses were carried out in a pyrolyser Rock-Eval 6, Vinci Technologies equipped with a flame ionization detector (FID).

Vitrinite reflectance determinations (%Ro)

Unheated sample and solid residues from steam pyrolysis were prepared for optical characterization. Mean random vitrinite reflectance (%Rrandom) measurements were carried out using a Leitz MPV3-SP microscope; 50x/0.85 oil immersion objective. Standards with known reflectance used were Sapphire 0.579%, Yttrium–Aluminium–Garnet 0.897% and Garnet–Gadolinium–Gallium 1.697%.

GC and GC–MS analyses

Aliphatic fraction of bitumen and whole expelled oil were run on a Hewlett–Packard 5890A gas chromatograph with a flame ionization detector (FID). Samples were injected (1 μ l) in the splitless mode with hydrogen as carrier gas. The oven was programmed for an initial temperature of 55 °C for 2 min., followed by heating rates of 30 °C/min (55–190 °C), 1.5 °C/min (190–250 °C) and 2.0 °C/min to a final temperature of 300 °C. The chromatography column was a high-resolution capillary column model J&W Scientific DB-5 (30 mx0.25 mm i.d., film thickness 0.25 μ m).

GC–MS analyses were carried out on aliphatic fractions from bitumen and expelled oils. The fractions were run on a gas chromatography Hewlett–Packard model 5890/II with a high-resolution capillary column model J&W Scientific DB-5 (30 mx0.25 mm i.d., film thickness 0.25 μ m), connected to a HP-5870MSD mass spectrometer operating at 70 eV and selected-ion-monitoring (SIM). The SIM saturate analyses focused primarily on m/z 217 (steranes) and m/z 191 (terpanes).

RESULTS AND DISCUSSION

Discriminations by source rock parameters (TOC, S₂, Tmax and %Ro)

The trends of TOC, Rock-Eval pyrolysis parameters (S₂ peak and Tmax) and vitrinite reflectance (%Ro) measurements obtained for the samples from the Lokpanta oil shale before and after the steam pyrolysis experiments are shown in Fig. 1. It is apparent that, as the time of interaction between the source rock and the vapor water at the maximum temperature (350 °C) increases, the TOC content decreases significantly (Fig. 1a), from 17.30 wt.% in the original sample to 5.16 wt.% after 18 h at maximum temperature.

However, a small increase in TOC content after this experimental time is also observed. A similar decreasing trend is observed for the S₂ peak, determined by Rock-Eval pyrolysis (Fig. 1b), whereas other parameters, such as Tmax and vitrinite reflectance used to evaluate the thermal evolution of the organic matter increase (Fig. 1c and d). The trend of reduction in TOC content (Fig. 1a) is explained by the fact that more and more organic matter is converted into petroleum products as exposure to maximum temperature increases.

At the same time the S₂ peak decreases, since there is less organic matter available for the generation of hydrocarbons. This decreasing trend is observed until experimental time for 18 h. At longer experimental times the S₂ peak remains constant (Fig. 1b) suggesting that the kerogen in the sample has reached the highest possible decomposition level for generation of hydrocarbons.

The Rock-Eval temperature of maximum hydrocarbon generation (Tmax °C) employed as a maturity parameter for source rocks, increased with the time of exposure to maximum temperature (350 °C), as shown in Fig. 1c. This pattern was expected and represents an increase in the thermal evolution of the organic matter present in the samples. The original sample has a Tmax value of 433 °C, indicative of the transition from the immature to mature zone for petroleum generation (Tissot and Welte, 1984). As the time of steam pyrolysis experiments was increased, Tmax values increased to more than 450 °C in the experiments with 36, 72 and 98 h, which corresponds to the final mature zone in the oil window. This increase in maturity, as indicated by Tmax, was also confirmed by the vitrinite reflectance value (%Ro) (Fig. 1d), ranging from 0.26%Ro in the original sample to 1.18%Ro in the experiments with 72 and 98 h.

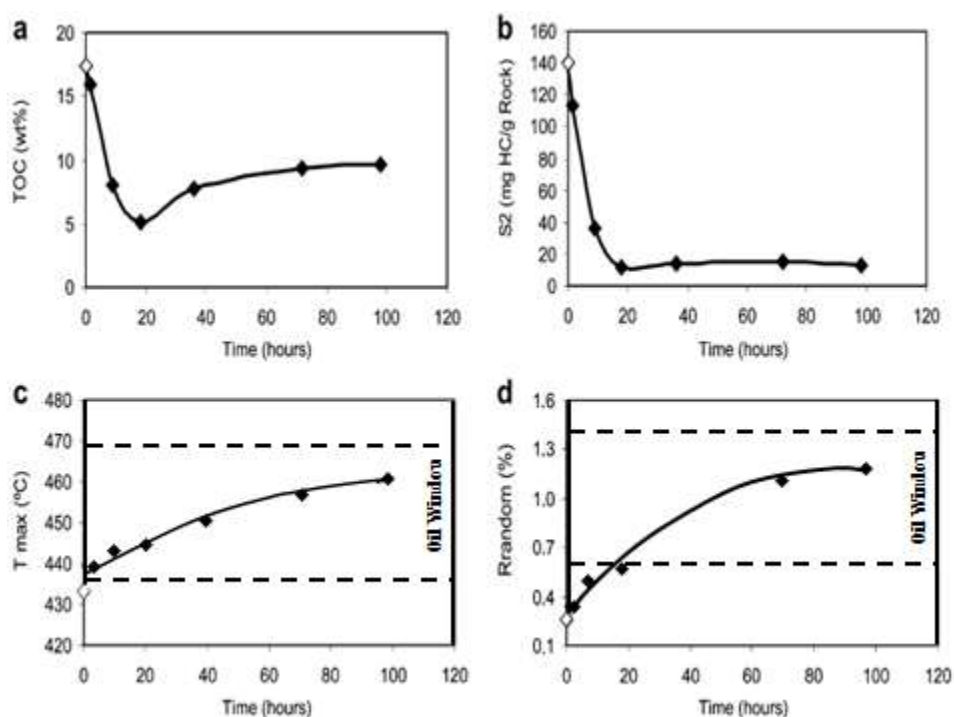


Fig. 1: Changes in: (a) TOC content, (b) Tmax, (c) S₂ peak and (d) vitrinite reflectance (%Ro) related to the increasing of the experimental time. Open diamonds represent the original sample (unheated).

The hydrogen index (HI) is commonly used as a parameter to determine the type of kerogen in early mature samples and to estimate the organic matter thermal evolution (Espitalié et al., 1977; Peters et al., 1986). In our study the hydrogen index (HI) value of 812 mg HC/g TOC determined in the original sample prior to pyrolysis indicates type I kerogen, and it can be clearly seen that this parameter decreases with the increase of the experimental time (Fig. 2). This trend is also observed for changes of the n-alkanes profile, as showed in Fig. 2.

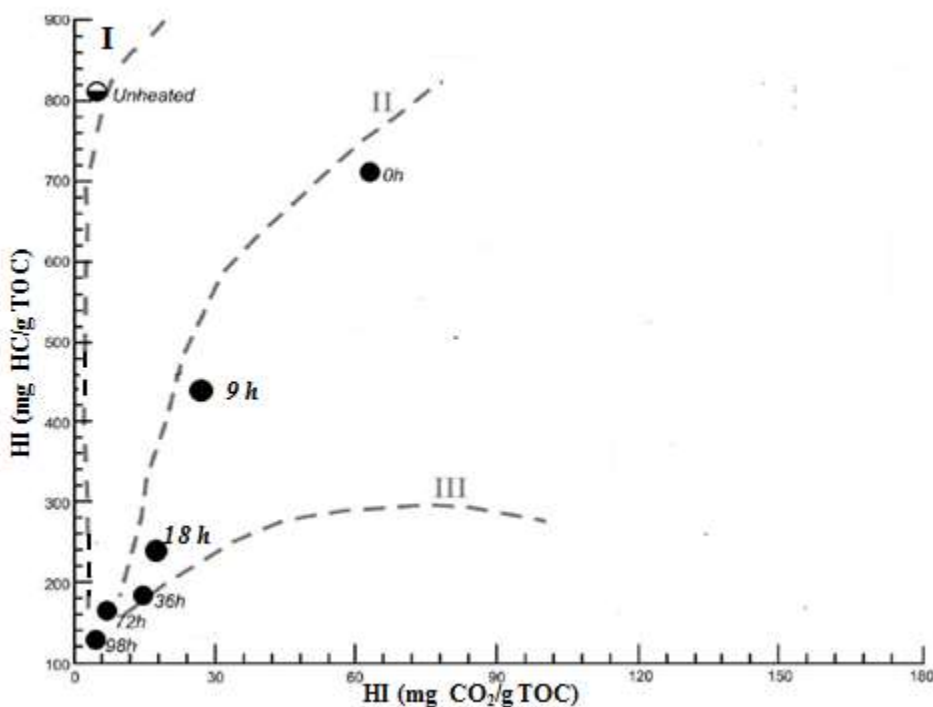


Fig. 2: Trends of the hydrogen index (IH), oxygen index (OI) and alkanes profile with the increase of the steam pyrolysis time at 350 °C.

Determination of the transformation ratio (TR) based on parameters from Rock-Eval analysis and TOC measurements (Table 1), show that TR increased regularly with increasing exposure time to maximum temperature, with a significant increase in experiments carried out between 0 and 18 h (TR = 17% and 74%) and a less significant increase with values ranging from 74% to 86%, for experiments lasting longer than 18 h. Since crushed rock samples (0.1–0.2 cm size) were used in our experiments, the TR values may actually be higher than those expected for larger fragments or blocks which would be more representative of natural conditions of petroleum generation in a basin environment.

The observed TR values were high for samples having vitrinite reflectances lower than 0.6%Ro. The discrepancy may be explained by the fact that vitrinite reflectances are suppressed by the presence of alginite compounds (Espitalié et al., 1993; Hutton and Cook, 1980; Kalkreuth and Macauley, 1987). Inter-laboratory exercise on the Lokpanta oil shale by the ICCP (International Committee of Coal and Organic Petrology) has shown that other maturity parameters such as lambda max and Q from spectral fluorescence measurements, Tmax from Rock-Eval analysis and the C₂₉ steranes 20S/ (20S + 20R) ratio all confirm a higher maturity level as indicated by vitrinite reflectance measurement (Borrego et al., 2006).

The studied sample of the Lokpanta oil shale contained a quite labile type I kerogen that probably generated petroleum in a rather narrow range of kinetic activation energies (Araujo, 2001). Being relatively fast under the steam pyrolysis conditions, the increase in petroleum generation and transformation ratio of the kerogen in the Lokpanta oil shale is not steadily accompanied by vitrinite

reflectance, which undergoes an increase under much slower kinetic parameters. This apparent discrepancy is more evident under experimental conditions requiring higher temperatures to compensate for the short time periods.

Table 1: Results of crushed and aliphatic fractions for generated bitumen (Bit.) and expelled oils (EO) after steam pyrolysis at 350 °C and 2100 psi in Lokpanta oil shale

Analytical time (h)	S ₁ /(S ₁ + S ₂) (%)	TR ^a (%)	Aliphatics		Aromatics		NSO		Pr/Ph		Pr/n-C ₁₇		Ph/n-C ₁₈		CPI ^b	
			Aliphatics (%)		Aromatics (%)		NSO (%)		Pr/Ph		Pr/n-C ₁₇		Ph/n-C ₁₈		CPI ^b	
			Bit.	EO	Bit.	EO	Bit.	EO	Bit.	EO	Bit.	EO	Bit.	EO	Bit.	EO
Unheated	3.00	0.00	44.00	0.00	20.00	0.00	36.00	0.00	1.53	0.00	2.00	0.00	3.15	0.00	1.72	0.00
0.00	6.00	17.00	27.00	29.00	21.00	41.00	52.00	30.00	1.56	1.66	2.20	2.38	2.20	2.58	1.81	1.35
9.00	8.00	54.00	24.00	19.00	26.00	37.00	50.00	44.00	1.87	1.92	1.92	1.75	1.59	1.26	1.11	1.05
18.00	16.00	74.00	19.00	32.00	28.00	29.00	53.00	39.00	2.00	2.23	1.37	1.36	1.15	0.87	1.11	1.19
36.00	11.00	77.00	23.00	36.00	10.00	40.00	67.00	24.00	2.00	2.88	0.82	0.88	0.64	0.67	1.15	1.08
72.00	24.00	84.00	25.00	32.00	15.00	45.00	60.00	23.00	2.12	2.76	0.75	1.02	0.52	0.72	1.05	1.06
98.00	22.00	86.00	15.00	30.00	31.00	38.00	54.00	32.00	1.93	3.22	0.92	1.02	0.70	0.48	1.04	1.08

NSO = (nitrogen, sulfur, oxygen); Pr (pristane); Ph (phytane); Bit. (bitumen); EO (expelled oil).

^a %TR (transformation ratio) = $\{[(HI_o - (HI_r \times TOC_r))/TOC_o]/HI_o\} \times 100$. The subscript ‘‘o’’ and ‘‘r’’ represent the values of the original and crushed samples, respectively. The TR formula, as proposed by Espitalié and Bordenave (1993), considers the amount of generated petroleum as the difference between the original and the residual hydrogen indices.

^b CPI (Carbon Preferential Index) = $\frac{1}{2}[(RC_{25} - C_{33}/RC_{24} - C_{32}) + (RC_{25} - C_{33}/RC_{26} - C_{34})]$.

Gas chromatography

The gas chromatograms of bitumens show an increase in the relative abundance of low molecular weight n-alkanes with the increase of the experimental time at 350 °C in steam pyrolysis conditions, as observed in Fig. 2. The original sample shows a low abundance of n-alkanes, regardless of their molecular weight. The gas chromatogram of the original sample (unheated) also shows a greater abundance of the isoprenoids pristane (Pr) and phytane (Ph), when compared to the n-alkanes C₁₇ and C₁₈, as well as an abundance of biomarker compounds. Both features being characteristic of a low maturity level (Mackenzie et al., 1984; Thomas et al., 1985).

The relative abundances of n-alkanes with low to medium molecular weight (n-C₁₄–n-C₂₀), as well as the heavier n-alkanes (n-C₂₁–n-C₄₂), increase with the time of the experiments (Fig. 2). This increase is caused by thermal cracking of the heavier molecules, such as the substituted aromatic compounds, resins, asphaltenes and cyclic compounds. With the increase in exposure time to maximum temperature (350 °C), significant changes also occur in the relative abundance of the isoprenoids pristane and phytane and C₁₇ and C₁₈ n-alkanes. Relative abundance of pristane and phytane is higher than C₁₇ and C₁₈ n-alkanes in experiments up to 18 h, whereas C₁₇ and C₁₈ n-alkanes predominate in experiments that lasted more than 36 h.

Comparing the chromatograms of the expelled oil and bitumens (Fig. 3), it is apparent that at relatively low maturation level (experiment for 0 h), the expelled oil is richer in low molecular weight n-alkanes than the bitumen, suggesting a somewhat higher maturity level for the expelled oil as compared to its bitumen counterpart in the source rock, as expected. However, at higher maturity levels (experiment for 72 h) the chromatograms of bitumen and expelled oil are very similar. Based on the variations observe) in the chromatograms from Fig. 3, it can be suggested that oils expelled by the source rocks at a low maturity levels tend to show a higher thermal evolution than the corresponding bitumen.

However, for samples with a higher thermal evolution, such differences were not noticed. Affected by the thermal evolution are also the pristane/phytane, pristane/n-C₁₇ and phytane/n-C₁₈ ratios and the Carbon Preferential Index (CPI) in the bitumen and expelled oil (Table 1). By increasing the experimental time the pristane/phytane ratio increases in bitumen and expelled oil, while pristane/n-C₁₇, phytane/n-C₁₈ and the CPI values decrease as expected.

The increase in the pristane/phytane ratios with increasing of the experimental time is due to greater stability of pristane as compared to phytane, which results in the relatively high relative increase of C₁₇ and C₁₈ n-alkanes in respect to pristane and phytane isoprenoids occurs, resulting in smaller values for these ratios as maturity increases, as showed in Fig. 2 under steam pyrolysis conditions. The Carbon Preferential Index (CPI) decreases in both bitumen and expelled oil as a function of the experimental time, due to the preferential thermal cracking of molecules with an odd number of carbon atoms over those with an even number (Hunt, 1995).

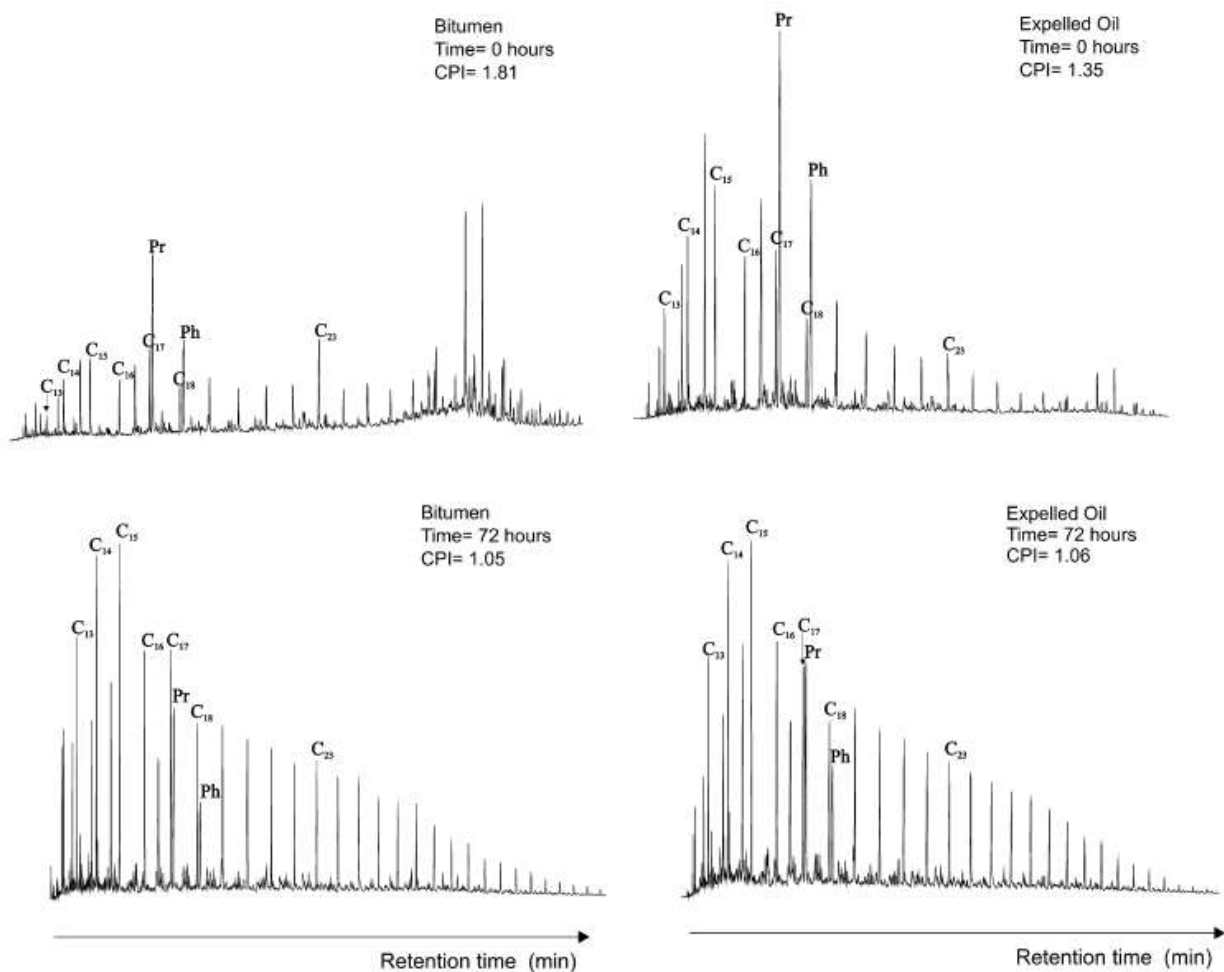


Fig. 3: Gas chromatograms of the aliphatic fraction showing the n-alkanes distribution of the bitumen (left column) and expelled oil (right column) obtained after steam pyrolysis at 350 °C for 0 and 72 h.

The trends found for the n-alkanes profile and for the ratios calculated from isoprenoids and n-alkanes in bitumens as well as expelled oils in the presence of water steam were similar to those reported for natural and hydrous pyrolysis conditions (Lewan et al., 1986; Alsaab et al., 2007; Koopmans et al., 1998; Monthioux et al., 1986; Monthioux et al., 1985; Soldan and Cerqueira, 1986; Elie and Mazurek, 2008).

Biomarker maturity ratios

Some biomarker ratios, which are considered to be indicators of organic matter maturity levels, such as the 22S/(22S + 22R) ratio of C₃₁ and C₃₂ homohopanes showed a slight trend to increase with increasing experimental time (Fig. 4a), whereas the 20S/(20S + 20R) and $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ C₂₉ sterane ratios show a much stronger trend (Fig. 4b). However, these ratios did not reach their equilibrium values. On the other hand, it can be observed in Fig. 4c that the Ts/(Ts + Tm) ratio tends to decrease although the opposite was expected (Hunt, 1995).

The increase of the 22S/(22S + 22R), 20S/(20S + 20R) and $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ ratios is frequently interpreted to be related to the mechanism of isomerization of the less stable biological configuration (22R, 20R, $\alpha\alpha\alpha$) to the more stable biological configuration (22S, 20S $\alpha\beta\beta$) during the geological diagenesis process (Mackenzie et al., 1981; Mackenzie and Mackenzie, 1983; Seifert, 1978; Seifert, et al., 1978). This same isomerization mechanism is proposed for the isomers Tm and Ts (Ts is more stable under geological conditions). However, a qualitative analysis of the chromatograms for the m/z 191 of the original samples and after experiments for 98 h, shown in Fig. 5, suggest that the observed trend for the Ts/(Ts + Tm) ratio is result of the concentration increase of the isomer Tm liberated from the kerogen, with the increase of the experimental time, without isomerization to the more stable Ts compound.

Studies by Farrimond et al. (1998) and Dzou et al. (1995) showed that the compound liberation rates from kerogen and the preferential degradation of one isomer over the other may influence the aforementioned trends. Taking into account that the purpose of the present work was to observe the behavior of the biomarkers ratio under water steam conditions and not the quantification of the compounds, it was not possible to establish the influence of those liberation rates and degradation with the data set created in the present study.

Effect of maturity on hopane and sterane distribution

Observing the trends in the ratios tricyclic/pentacyclic terpanes (Fig. 4d) and hopanes/steranes (Fig. 4e) it can be noticed that the increase of the steam pyrolysis time promoted the cracking of the higher molar weight molecules. This effect was more pronounced for steranes than for hopanes (Fig. 5), and confirms earlier studies by Eglinton and Douglas (Eglinton and Douglas, 1988). On the other hand, the inversion in the relative abundance of the C₂₇ and C₂₉ steranes in longer experiments (36 and 72 h) was also observed. The C₂₇ and C₂₉ steranes show a distinct pattern with an increase in C₂₇ and a decrease in C₂₉ steranes with increasing experimental time (Fig. 4f), whereas the C₂₈ steranes remained unchanged.

The increase observed in the relative content of the C₂₇ steranes can be attributed to preferential thermal cracking of the C₂₉ steranes, which occurs during the thermal evolution of the organic matter. The variations in the abundance of C₂₇ and C₂₉ steranes related to the level of maturity have implications on the interpretation of the organic matter source affecting the information that can be obtained from these, e.g. in immature organic matter the greater abundance of the C₂₇ sterane suggests a planktonic or marine source, whereas the predominance of the C₂₉ sterane is considered to indicate contribution from terrestrial plants (Peters et al., 2005; Hunt, 1995). Since these parameters are affected by temperature care should be taken when the steranes abundance is used in the interpretation of depositional environments.

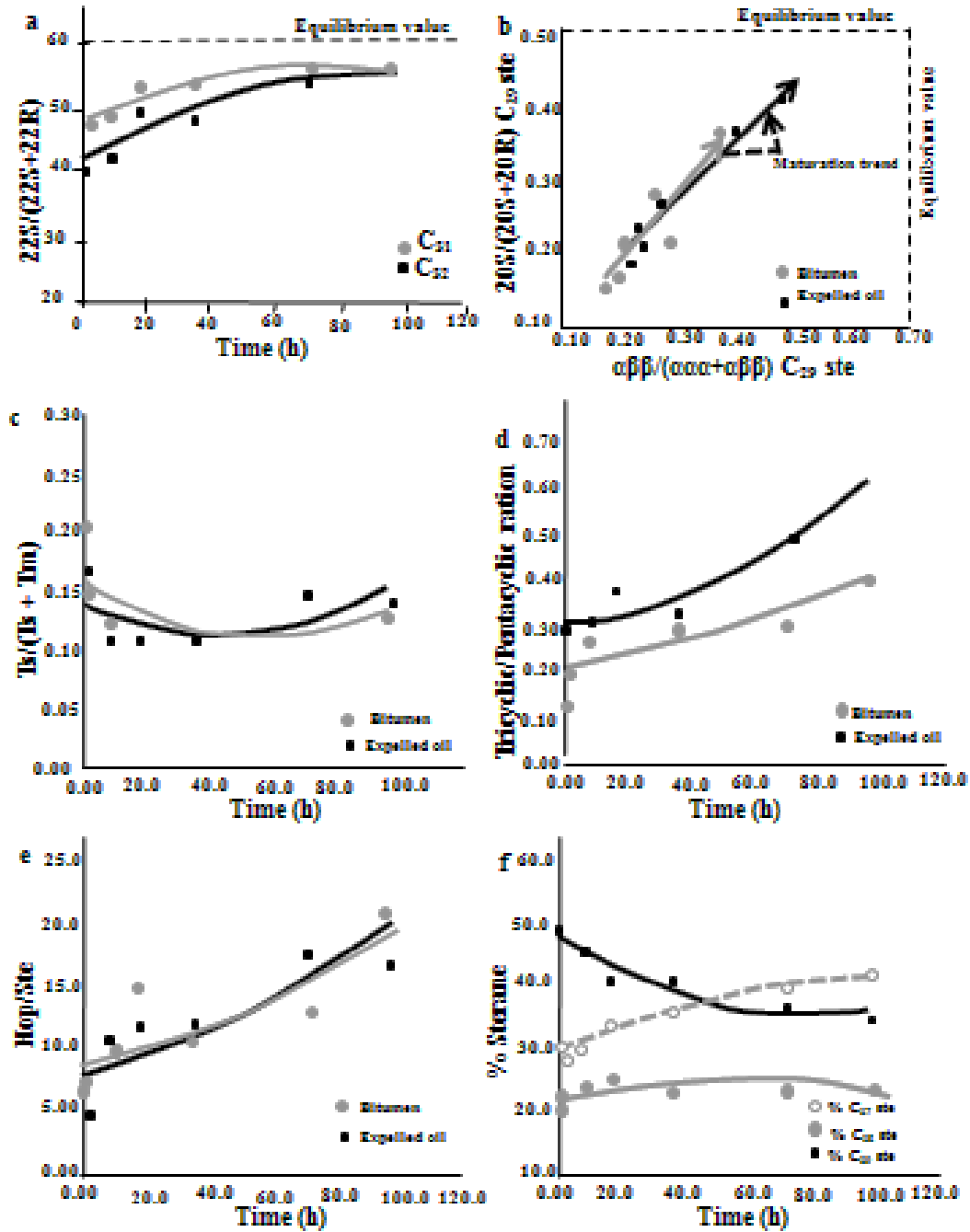


Fig. 4: Trend of the ratios used to establish maturity level, (a) 22S/(22S + 22R) of C₃₁ and C₃₂ homohopanes, (b) 20S/(20S + 20R) of C₂₉ sterane, (c) Ts/(Ts + Tm), (d) tricyclic/ pentacyclic ratios, (e) organic matter source hopane/sterane ratio and (f) percentage of C₂₇, C₂₈ and C₂₉ sterane with the increase of the experimental time at 350 °C.

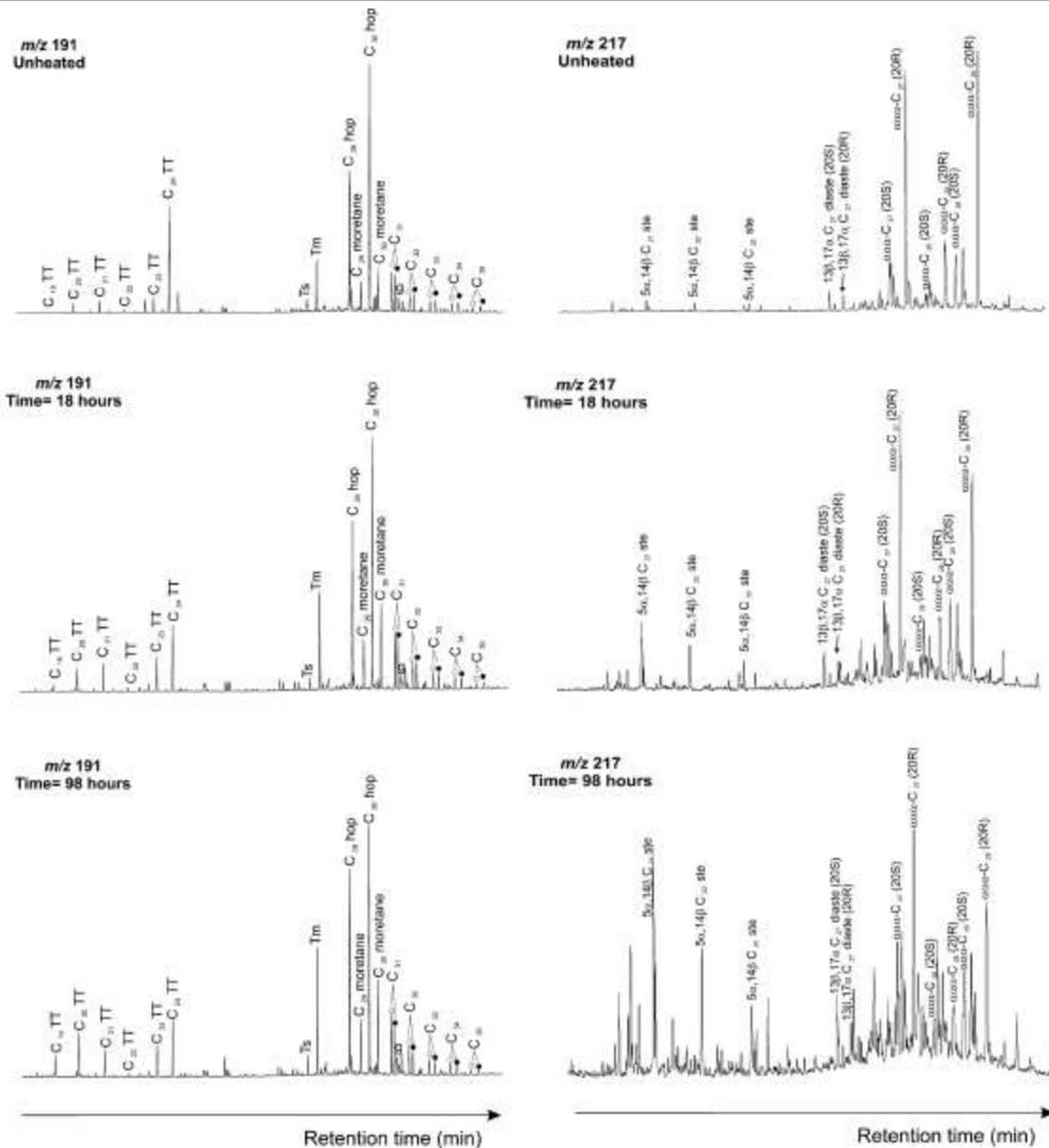


Fig. 5: m/z 191 and m/z 217 Mass chromatograms of the bitumen from the unheated sample and solid residues from steam pyrolysis at 350 °C for 18 and 98 h of oil shale from Lokpanta. TT = tricyclic terpene, g = gammacerane, empty and filled dots indicate (22S) and (22R)-17 α , 21 β (H) isomers, respectively.

Composition of bitumen and expelled oil

The chemical composition of bitumen and expelled oils (Table 1) showed that: (i) the amounts of aliphatic, aromatic and NSO compounds (resins and asphaltenes) in the bitumen extracted from the solid residues vary significantly, when compared to the bitumen extracted from the original sample; (ii) the increase of the experimental time do not affected significantly the chemical composition both expelled oil and bitumen as expected (an increase of the aliphatic and aromatic fractions relative to the decrease of polar compounds with the increase of maturity level as showed by Tissot & Welte (1984); and (iii) when the composition of expelled oil and bitumen are compared, the percentages of aliphatics and aromatics, in the expelled oils, are always greater than those in the bitumen, whereas the heaviest fraction (resins and asphaltenes or NSO) is less abundant. This difference in the chemical composition of expelled oil and

bitumen has also been reported for hydrous pyrolysis conditions (Lewan, 1993; Peters et al., 1990) and natural sequences (Tissot and Welte, 1984; Peters et al., 2005).

Table 1 show that bitumen extracted from the unheated sample presents aliphatic and polar (NSO) fractions in almost identical amounts, while bitumens generated during experiments present an aliphatic fraction much smaller than the polar one. This difference can be attributed to the fact that increasing in temperature generates, initially, bitumens with chemical composition enriched in heavier compounds (NSO) (Lewan, 1993; Tissot and Welte, 1984; Peters et al., 2005). On the other hand, the difference in chemical composition between bitumens and oils is due to the preferential retention in the rock of polar compounds (NSO) when compared to aliphatic and aromatic compounds during the primary migration process. During the primary migration the chemical composition of expelled oils is relatively enriched in aliphatic and aromatic hydrocarbons which are less retained by the source rocks, resulting bitumen with a smaller fraction of these compounds and enriched in the heavier and polar fraction (resins and asphaltenes or NSO). The preferential retention of resins and asphaltenes by the source rock occurs because these compounds are macromolecules with high molar masses and with heteroatoms (NSO) as part of their structures conferring a significant polarity and a strong interaction with the matrix.

CONCLUSIONS

Based on the pyrolysis experiments at 350 °C in the presence of water steam showed that increasing of the experimental time results in increase of the maturation level of organic matter in the Lokpanta oil shales. The Tmax (°C) values and vitrinite reflectances (%Ro) showed that during the longest experimental time used (98 h); the maturity level of the rock reached the end of the oil generation window. However, the biomarker ratios from hopanes and steranes (22S/(22S + 22R), 20S/(20S + 20R) and $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$, determined in bitumens and expelled oils generated, did not reach the equilibrium values, suggesting that the experimental conditions had a significant effect on geochemical and petrographical parameters of the solid residues when compared with the biomarkers ratios of the liquid products.

Maturity levels in the expelled oil based on n-paraffin distributions (gas chromatograms) may indicate an elevated maturity level, which does not correspond to the maturity level of the bitumen in the source rock, where the expelled oil was generated. These differences decrease with increasing maturity.

Biomarker ratios used to interpret depositional environments, like the pristane/phytane ratio, the hopanes/steranes ratio and the distribution of C₂₇, C₂₈ and C₂₉ steranes, were also affected by the experimental conditions.

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