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## Aromatic steroids as a tool in geochemical interpretation

The article describes the use of monoaromatic (MAS) and triaromatic (TAS) steroids in geochemical interpretation. So far for correlation purposes in crude oil–oil systems and crude oil–source rock, among others, biomarkers from the hopanes and steranes group or phenantrene compounds were used. Steroids can be used with equally good results as indicators of environmental sedimentation of organic matter, or a degree of thermal maturity of source rock. Steroids also find use as a carrier of information about: the genesis of organic matter (marine or non-marine) and immersion of carbonates in sediment or salinity of a sedimentary environment. The article presents the composition of triaromatic and monoaromatic steroids in samples of potential source rocks represented by: Menilite Beds of the Skole Unit, Main Dolomite of the Polish Lowland, Peribaltic Syncline Silurian and Central Atlantic Margin (CAM).

**Key words:** Monoaromatic steroids (MAS), triaromatic steroids (TAS), the geochemical correlation, sedimentation environment, the degree of thermal maturity.

### Aromatyczne steroidy jako narzędzie w interpretacji geochemicznej

Niniejszy artykuł opisuje zastosowanie monoaromatycznych (MAS) i triaromatycznych (TAS) steroidów w interpretacji geochemicznej. Dotychczas w celach korelacyjnych w układach: ropa naftowa–ropa naftowa i ropa naftowa–skała macierzysta wykorzystywano m.in. biomarkery z grupy hopanów i steranów czy związki fenantrenowe. Steroidy mogą być stosowane z równie dobrym skutkiem, jako wskaźniki środowiska sedymentacji materii organicznej, czy stopnia dojrzałości termicznej skały macierzystej. Steroidy znajdują także zastosowanie, jako nośnik informacji o: pochodzeniu materii organicznej (morskie lub niemorskie) oraz udziale węglanów w osadzie lub stopniu zasolenia środowiska sedymentacji. W artykule przedstawiono skład triaromatycznych i monoaromatycznych steroidów w próbkach potencjalnych skał macierzystych reprezentujących: warstwy menilitowe jednostki skolskiej, dolomit główny Nizy Polskiego, sylur Synklizy Perybaltyckiej oraz z wierceń w dnie oceanicznym w rejonie afrykańskiego szwu kontynentalnego.

**Słowa kluczowe:** Monoaromatyczne steroidy (MAS), triaromatyczne steroidy (TAS), korelacja geochemiczna, środowisko sedymentacji, stopień dojrzałości termicznej.

### Introduction

The biomarkers are organic compounds found in the source rock and crude oils, based on which the sedimentary environment, the type of organic matter in source rock, the degree of thermal maturity or geological age can be determined. The information from the analysis of biomarkers can be used for the correlation of oils in terms of oil–to oil.

Identifying the presence and determining the composition of specific biomarkers groups and their isomers in dispersed organic matter (DOM) contributes to learning the thermal history of sedimentary petroleum basins which has

a crucial meaning in the modeling of oil systems. Nowadays, for the analysis of source rock and reservoir fluids, the geochemical results evaluated from saturated fraction biomarkers like: penta and tricyclic terpenes, steranes and diasteranes as well as sulfur and phenantrene compounds present in aromatic fraction are useful for the assessment of its thermal evolution. Part of the maturity parameters can successfully relate to the value of vitrinite reflectance, which is an absolute measurement of the thermal maturity (transformations) [6].

The method was developed to identify other groups of compounds present in aromatic fraction – partially or completely aromatized steroids using a variety of source rock samples differentiated by the type of kerogen and the level of thermal maturity and geological age. For this purpose core samples of source rock were selected, represented by Menilite Beds of the Skole Unit, Main Dolomite of Lowland, Peribaltic Syncline Silurian and ocean drilling in the Central Atlantic Margin.

Steroid test results have been presented together with the results of other groups of biomarkers, which allowed for the association of genetic and paleoenvironmental traits of individual stratigraphic series with the presence of steroids and their structural changes together with the progressive evolution of diagenetic and thermocatalytic processes.

Monoaromatic (MAS) and triaromatic (TAS) steroids are aromatic and saturated hydrocarbon compounds. C-ring monoaromatic steroids (MAS) are comprised of two cyclohexane rings (A + B) and one cyclopentane ring (D-ring) fused with an aromatic ring (C-ring) in their molecular structure. Triaromatic steroids (TAS) have a similar molecular structure to MAS and the main difference is that their cyclohexane rings A and B are replaced by aromatic rings (Figure 1). Their concentration in geological samples is relatively low but their resistance to the degradation process makes them useful for the geochemical interpretation in correlation characteristics, and in the identification of paleoenvironmental sedimentological conditions as well.

TAS-cholestanes ( $C_{26}$ ), TAS-ergostanes ( $C_{27}$ ) and (TAS- $C_{28}$ ) stigmastanes are the most recognizable triaromatic steroids (TAS) in most geological samples.  $C_{26}$  TAS-cholestane (20R) and  $C_{27}$  TAS-ergostane (20S) coelute with each other

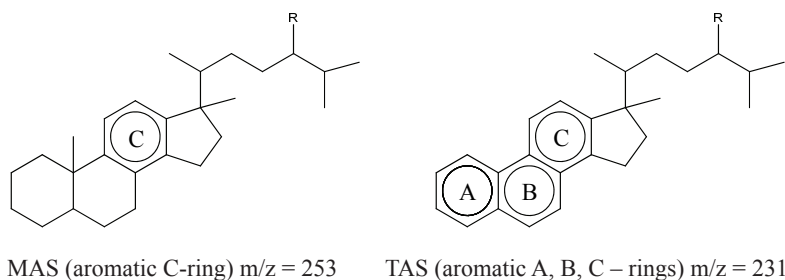


Fig. 1. Structures of mono- and triaromatic steroids

and often occur as the highest peak in the chromatogram of  $m/z = 231$  [4].

In catagenetic processes, monoaromatic steroids (MAS) are transferred into triaromatic hydrocarbons (TAS), (Figure 2).

The aromatic steroids shown in Figure 2, are the result of the progressive diagenesis evolution and the thermal evolution of sterols, which are present in the sedimentary organic matter. In samples with low maturity one can often next to triaromatic steroids (TAS), also identify monoaromatic steroids (MAS).

The geochemical interpretation based on the structure of steroids leads to the evaluation level of the diagenetic and thermal processes [5, 7, 8].

In literature there are many references about the use of the structure of monoaromatic steroids (MAS) and triaromatic steroids (TAS) to differentiate the type of organic matter. For this purpose as well as for regular steranes the triangular diagram  $C_{27}:C_{28}:C_{29}$  MAS is used [7, 9]. The other type of indicators calculated from the distribution of mono- (MAS) and triaromatic steroids (TAS) are the ratio TAS/MAS and the relative content of the compounds of the short and long sided hydrocarbon chain MAS and TAS.

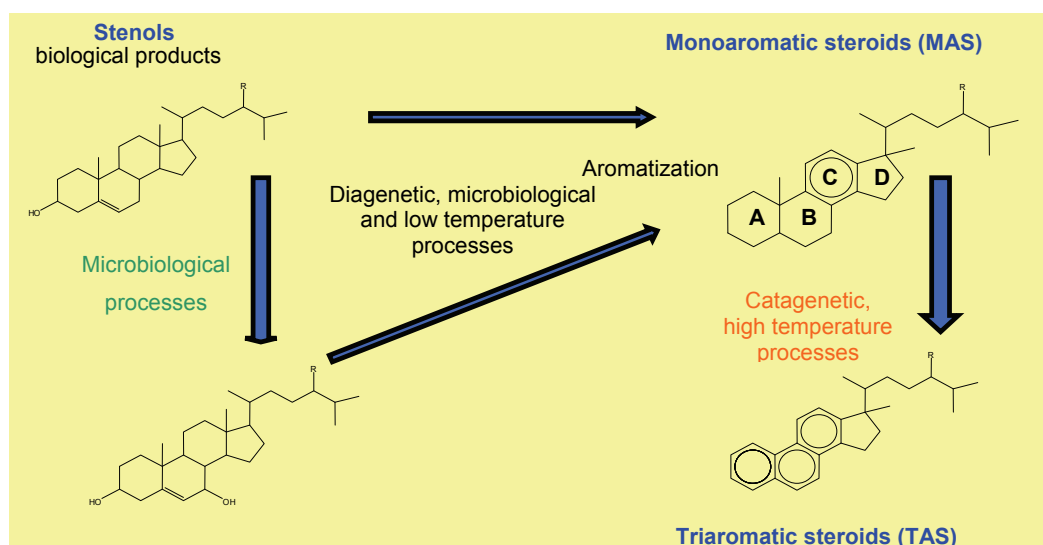


Fig. 2. Diagram showing further structural changes of sterols in the sedimentary organic matter leading to the formation of MAS and TAS structures

The aromatic fraction may also be important in determining the sedimentary environment and the type of biological precursors being part of the sedimentary organic matter. Of course it is possible that not all compounds found in geological samples can be related to primary producers. This uncertainty refers to e.g. methyl derivatives of mono- and triaromatic steroids [1, 3],

which probably may have their origin among ocean eukaryotes. Most of the sterols which are associated with the occurrence of eukaryotes (under the influence of structural transformation during a geological history), are reduced and aromatized. However, the structure of methyl derivatives of triaromatic steroids, could not be connected with known living organisms.

### Methodology of steroids researches

#### Extraction and SARA separation of organic matter

Bitumen extraction from rock was performed on approximately 100 g of the powdered samples using a Soxhlet apparatus with an azeotropic mixture of dichlorometane (DCM) and methanol (CH<sub>3</sub>OH) (93:7). The extraction was carried out for approx. 24 hours. The obtained extracts (EOM) were concentrated, by vaporization of the excess solvent, while the extracts were prevented from drying. The acquired extracts were quantitatively transferred to weighed bottles and extract yield was determined. Then, having been percolated through a filter, the solution was transferred to a new bottle, and the excess solvent was evaporated as it was done before. The results regarding the extracted bitumens were given in ppm. The comparative range of result error, in the given conditions is 10% of the weight of the extract.

Asphaltenes were precipitated with the use of n-hexane, and the obtained maltene solution was separated SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> by column liquid chromatography into aliphatic, aromatic hydrocarbons, and resins on packed columns. The columns were filled with a mixture of silica gel and aluminum oxide (2:1). Before application, aluminum oxide had been activated for 4 hours at 800°C; silica gel (0.2÷0.5 mm) had been activated for 12 hours at 160÷180°C.

Saturated hydrocarbons were eluted with n-hexane, aromatic hydrocarbons – with a mixture of n-hexane and toluene (1:3), and resins – with a mixture of dichloromethane and methanol (1:1) [2].

#### GC/MS method

An analysis of specifically saturated and aromatic biomarkers was conducted using the gas chromatography technique

coupled with Polaris Q mass spectrometer equipped with Rtx-5MS column (30 m × 0.25 μm × 0.25 mm).

The applied temperature program was as follows: initial temperature of 60°C, isotherm 1 minute, then temperature increase up to 310°C (isotherm 15 minutes) at rate of 4°C/min.

The obtained mass spectrograms of the saturated fraction and aromatic fraction of the analyzed samples in the total ion scan mode (TIC), in the mass interval of 50 to 650, were then subject to further computer processing, selecting mass spectrograms of definite classes of biomarkers for identification (m/z = 231, m/z = 245, m/z = 253).

#### Geochemical characteristics of core samples

The studies were conducted on selected samples of bituminous extracts (20 samples). Data of four of the most representative are in this work. All the samples tested were characterized by the presence of type II kerogen with varying quantities: TOC (from 0.19% in the main dolomite to 6.43% from Central Atlantic Margin) and the extractable organic matter (from 209 ppm to 31.050 ppm), (Table 1). The composition of the sample group was dominated by the saturated or resins fraction.

Genetic and maturity parameters based on all saturated and aromatic biomarkers including aromatic steroids (for selected samples represented by Menilite Beds, Skole Unit, Main Dolomite of Polish Lowland, Silurian Peribaltic Sineclise and Central Atlantic Margin are shown in Table 2.

In order to achieve the greatest amount of geochemical information the results based on the analyses of aromatic steroids should be considered with the characteristic of the biomarkers saturated fraction. Process of transformation of a different biomarker groups could be unevenly affected by

Table 1. Geochemical data for potential source rock analyzed for steroid distribution

Sample No.	Stratigraphy	TOC [%]	HI [mg HC/g of TOC]	T <sub>max</sub> [°C]	Extract yield [ppm]	Saturated [%]	Aromatic [%]	Resins [%]	Asphaltenes [%]
1.	Menilite/Oligocene	4.84	431	407	31 050	58.1	29.2	10.3	2.4
2.	CAM	6.43	293	433	13 673	19.7	24.0	45.5	10.8
3.	Main Dolomite	0.19	126	431	209	34.5	27.0	35.8	2.7
4.	Syneclise	1.49	320	440	1 826	39.2	34.6	24.9	1.3

TOC – Total organic carbon, HI – Hydrogen index,

Table 2. Geochemical indicators calculated based on the distribution of: n-alkanes, isoprenoids, steranes, hopanes and aromatic biomarkers for selected samples

Pr/ Ph	Pr/ n-C <sub>17</sub>	Ph/ n-C <sub>18</sub>	Steranes [%]			S/(S + R) C <sub>29aaa ster</sub>	$\beta\beta/(aa + \beta\beta)$ C <sub>29 ster</sub>	S/(S + R) C <sub>31hop</sub>	$T_x$ T <sub>m</sub>	$M$ C <sub>30 hop</sub>	R <sub>C1</sub> [%]	R <sub>C2</sub> [%]	C <sub>26</sub> /C <sub>28</sub> 20S	C <sub>27</sub> /C <sub>28</sub> 20R	C <sub>27</sub> /C <sub>28</sub> TAS
			C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>										
Menilite Beds															
2.17	1.00	0.51	45	22	33	0.40	0.48	0.56	0.97	0.14	0.71	0.68	0.50	1.08	1.08
Main dolomite															
0.56	0.44	0.77	36	30	34	n.c.	n.c.	0.55	3.65	0.42	1.03	0.91	n.c.	n.c.	n.c.
Peribaltic Syncline															
1.39	0.51	0.48	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.73	0.86	n.c.	0.25	0.23
African Continental Margins (The bottom of the ocean)															
1.05	1.75	1.88	35	38	27	0.40	n.c.	0.56	n.c.	0.24	n.c.	n.c.	0.90	1.14	1.21

n.c. = not calculated – to low level of biomarkers or insufficient resolution of the peaks; S/(S + R) C<sub>29 ster</sub> = ratio of the 20S and 20R epimers 24-etylo-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane; S/(S + R) C<sub>31 hop</sub> = ratio of the 22S and 22R epimers 17 $\alpha$ (H)21 $\alpha$ (H)-homohopane;  $T_x/T_m$  = ratio of the 18 $\alpha$ (H)-22,29,30-trisnorhopane and 17 $\alpha$ (H)-22,29,30-trisnorhopane; M/C<sub>30 hop</sub> = ratio of the 17 $\alpha$ (H)21 $\alpha$ (H)-hopane (moretane) and 17 $\alpha$ (H)21 $\alpha$ (H)-hopane. R<sub>C1</sub> [%] – calculated vitrinite reflectance (0.6 · MPI-1 + 0.4); R<sub>C2</sub> [%] – calculated vitrinite reflectance (0.073 · MDR + 0.51). C<sub>26</sub>/C<sub>28</sub> 20S – ratio of the C<sub>26</sub> Triaromatic Sterane (20S) and C<sub>28</sub> Triaromatic Sterane (20S). C<sub>27</sub>/C<sub>28</sub> 20R – ratio of the C<sub>27</sub> Triaromatic Sterane (20R) and C<sub>28</sub> Triaromatic Sterane (20R). C<sub>27</sub>/C<sub>28</sub> TAS – 2 · C<sub>27</sub> Triaromatic Sterane (20R) / (C<sub>28</sub> Triaromatic Sterane (20S) / C<sub>28</sub> Triaromatic Sterane (20R)).

time and temperature. Therefore, this will lead to contradictory results and it is connected with problems in unequivocal interpretation. Because of that, all information obtained from biomarker analysis need to be interpret jointly.

Most of the bitumens showed slightly different degree of thermal maturity, in the range between low layer maturity level for Menilite Beds, to the peak oil window for samples of Silurian Peribaltic Syncline (Table 2). Some of the samples did not contain a sufficient amount of the saturated fraction biomarkers useful, to calculate the ratios, so in particular in these cases it is preferred, to look for additional indicators, carrying genetic and maturity information (Figure 11b, 12a, 12b). This case refers to a sample of the Silurian, where pentacyclic terpenes and steranes occurred only in trace amounts (Figure 9a, 9b, 10a, 10b).

In the bitumen extracts samples from Menilite Beds of the Skole Unit with the lowest thermal maturity (based on the pyrolytic parameters), the presence of all the triaromatic steroids compounds was noticed (TAS) (Figure 6b). Distribution of TAS shows the same type of organic matter as represented by CAM sample, and a slightly lower degree of thermal maturity (Table 2). In some samples from Menilite Beds small amounts of monoaromatic steroids (MAS) were also found, which indicates that not all steroid structures were aromatized (low degree of thermal maturity) what is consistent with  $T_{max}$  parameter. The predominance of C<sub>26</sub>–C<sub>28</sub> in the composition of triaromatic steroids, indicates on dominance of marine organic matter (Figure 3b, 4b, 5b, 6b, 7b).

In the bitumen from the sample taken from the bottom of the ocean, which also showed relatively low thermal maturity (particularly in biomarker distribution (Figure 4a, 5a), triaromatic steroids (TAS) were presented in relatively large amounts (all seven compounds), (Figure 6a). There was no presence of monoaromatic steroids (MAS). This means that diagenetic processes are more advanced than in the Menilite Beds of the Skole Unit (Figure 3a, 7a).

In samples of bitumens from the Main Dolomite (Figure 8a), (which is characterized by reductive deposition environment conditions and also higher maturity), a minimal amount of triaromatic steroids were found as well as the absence of monoaromatic steroids. Samples from the Main Dolomite were characterized mainly by the presence of C<sub>20</sub>–C<sub>21</sub> TAS group, which corresponds well with a high content of C<sub>29</sub> norhopane, suggesting a high contribution of carbonate to the organic matter. This fact is very useful for correlation with petroleum existing in the Dolomite (Figure 8a, 9a, 10a, 11a, 12a).

The sample of bitumen of Lower Silurian which shows maturity in the oil window do not contain steranes and hopanes and therefore the relevant information was provided by the study of steroids. In this sample the presence of triaromatic steroids (TAS) was found. Their quantities were low with the dominant short chain C<sub>20</sub>–C<sub>21</sub> compounds. None of the samples showed the presence of monoaromatic steroids, which further confirms the high thermal maturity of the organic matter (Figure 8b, 9b, 10b, 11b, 12b).

**Central Atlantic Margin**

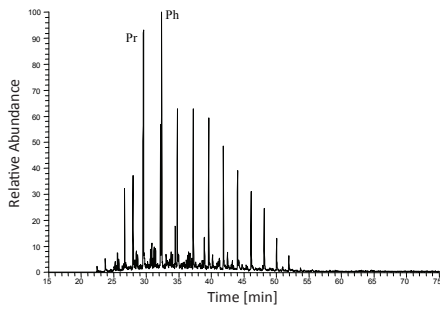


Fig. 3a. N-alkanes

**Menilite Beds**

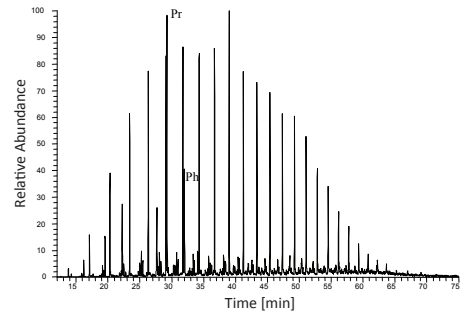


Fig. 3b. N-alkanes

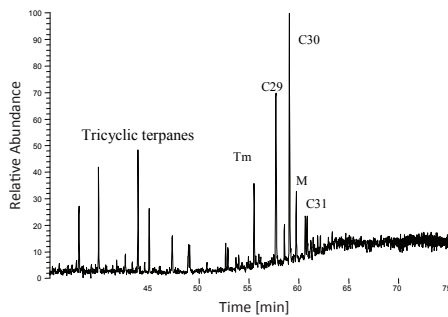


Fig. 4a. Hopanes (m/z 191)

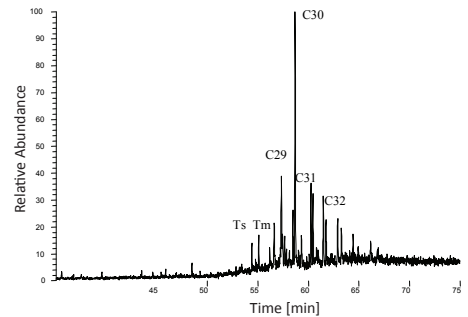


Fig. 4b. Hopanes (m/z 191)

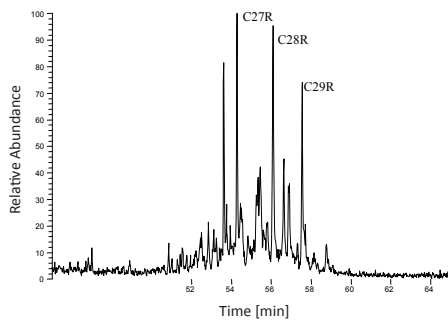


Fig. 5a. Steranes (m/z 217)

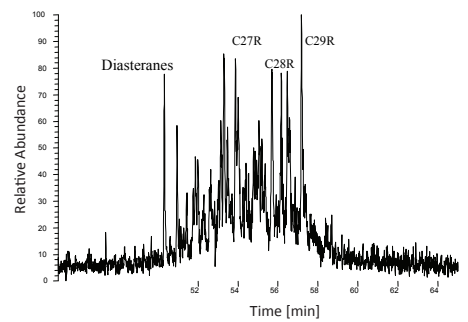


Fig. 5b. Steranes (m/z 217)

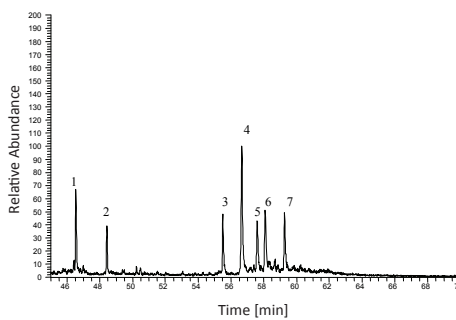


Fig. 6a. Triaromatic steroids (m/z 231)

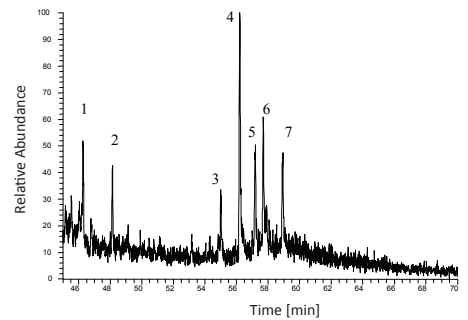


Fig. 6b. Triaromatic steroids (m/z 231)

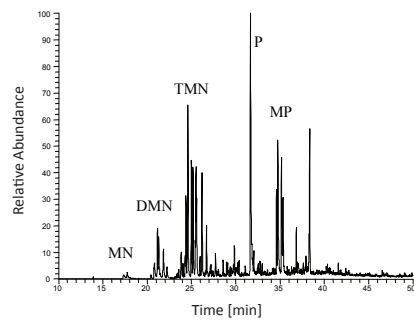


Fig. 7a. Aromatic biomarkers

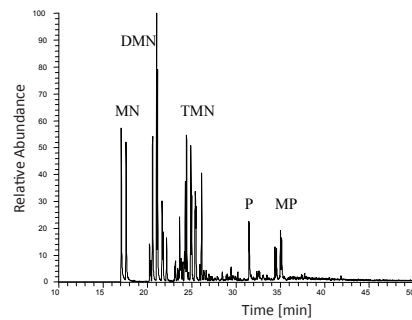


Fig. 7b. Aromatic biomarkers

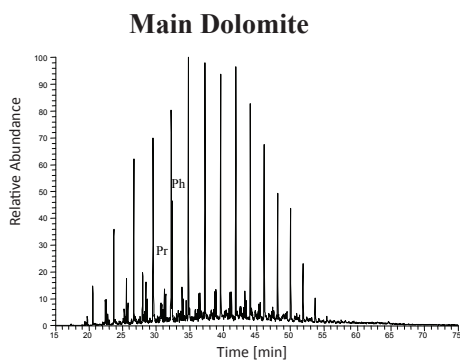


Fig. 8a. N-alkanes

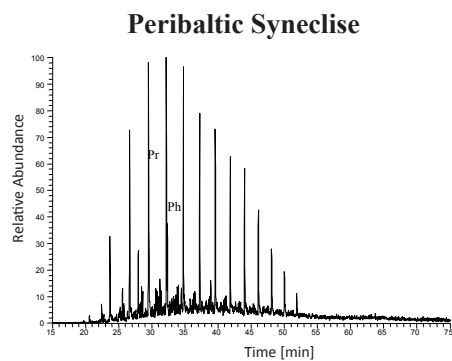


Fig. 8b. N-alkanes

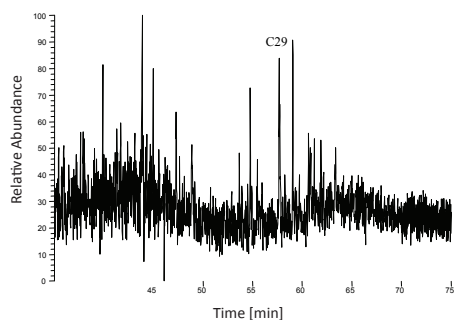


Fig. 9a. Hopanes (m/z 191)

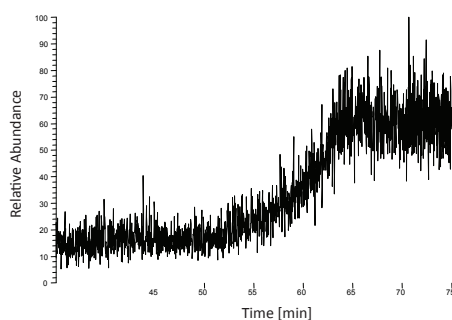


Fig. 9b. Hopanes (m/z 191, not present)

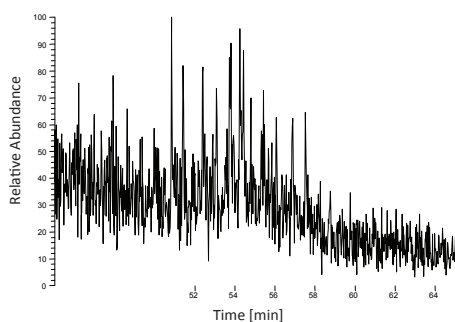


Fig. 10a. Steranes (m/z 217, trace amounts)

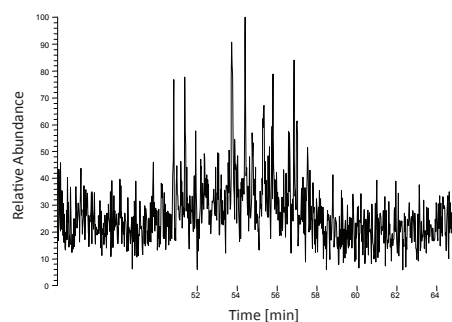


Fig. 10b. Steranes (m/z 217, trace amounts)

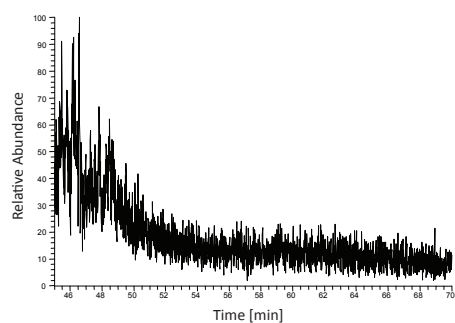


Fig. 11a. Triaromatic steroids (m/z 231)

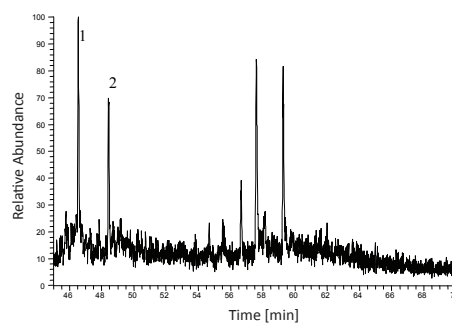


Fig. 11b. Triaromatic steroids (m/z 231)

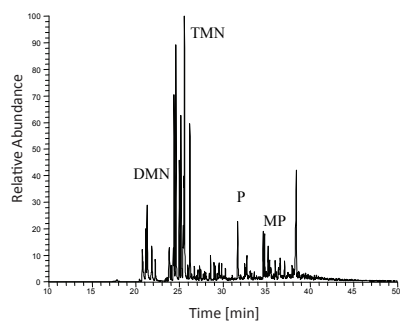


Fig. 12a. Aromatic biomarkers

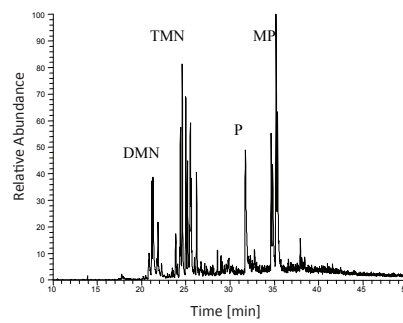


Fig. 12b. Aromatic biomarkers

**Peak description:**

Figures: 3a, 3b, 8a, 8b

Pr – Pristane

Ph – Phytane

Figures: 4a, 4b, 9a

$T_s$  –  $C_{27}18\alpha(H)-22,29,30$ -trisorneohopane

$T_m$  –  $C_{27}17\alpha(H)-22,29,30$ -trisnorhopane

$C_{29}$  –  $17\alpha(H)21b(H)-30$ -norhopane

$C_{30}$  –  $C_{30}17\alpha(H)21b(H)$ -hopane

$M$  –  $C_{30}17\beta(H)21\alpha(H)$ -moretane

$C_{31}$  –  $C_{31}17\alpha(H)21\beta(H)22(S)$ -hopane and

$C_{31}17\alpha(H)21\beta(H)22(R)$ -hopane

$C_{32}$  –  $C_{32}17\alpha(H)21\beta(H)22(S)$ -hopane and

$C_{32}17\alpha(H)21\beta(H)22(R)$ -hopane

Figures: 5a, 5b

$C_{27}R$  –  $C_{27}14\alpha(H)17\beta(H)20(R)$ -cholestane

$C_{28}R$  –  $C_{28}14\alpha(H)17\beta(H)20(R)$ -cholestane

$C_{29}R$  –  $C_{29}14\alpha(H)17\beta(H)20(R)$ -cholestane

Figures: 6a, 6b, 11b

1 –  $C_{20}$  Triaromatic Sterane

2 –  $C_{21}$  Triaromatic Sterane

3 –  $C_{26}$  Triaromatic Sterane (20S)

4 –  $C_{26}$  Triaromatic Sterane (20R) +  
 $C_{27}$  Triaromatic Sterane (20S)

5 –  $C_{28}$  Triaromatic Sterane (20S)

6 –  $C_{27}$  Triaromatic Sterane (20R)

7 –  $C_{28}$  Triaromatic Sterane (20R)

Figures: 7a, 7b, 12a, 12b

MN – methylnaphthalenes

DMN – dimethylnaphthalenes

TMN – trimethylnaphthalenes

P – phenantrene

MP – methylphenantrenes

## Summary

1. Twenty samples were analyzed in order to identification of aromatic steroids.
2. It was stated that the presence of monoaromatic steroids (MAS) is definitely restricted to samples with a lower thermal maturity. Therefore it is necessary to compile these observations with measurements of maturity by recognized geochemical indicators and establish limits, when the presence of these compounds is noticeable.
3. The presence of triaromatic steroids has been found (TAS) in a larger number of samples with marine origin verified,
4. The presence of triaromatic steroids (TAS) was observed at the lowest level in the bitumens, showing the highest maturity and low oxygen index.
5. High concentration of  $C_{29}$  norhopane suggest in situ origins of organic matter in investigated source rock. Dominance of  $C_{20}$ – $C_{21}$  group of triaromatic steroids (TAS) is an additional confirmation of above statement.

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