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PETROLEUM BIOMARKERS AS INDICATORS OF OIL ORIGIN AND MATURITY IN THE SOUTH-EASTERN PRECASPIAN BASIN

Abstract

This study investigates the origin of oil from the south-eastern Precaspian Basin through biomarker analysis of five crude oil samples using gas chromatography-mass spectrometry (GC-MS). Biomarkers serve as molecular fingerprints to elucidate hydrocarbon origin, source rock characteristics, and thermal history. The analyzed samples revealed: a marine depositional environment (C_{26}/C_{25} terpane ratios = 0.59–0.79), carbonate-dominated source rocks (C_{29}/C_{30} hopane ratios = 4.78–5.55), sourcing from Paleozoic (Permo-Carboniferous) strata (C_{28}/C_{29} sterane ratios = 0.44–0.57), and peak oil window – late maturation according to Ts/T, $C_{29}T_s$/ $C29T_m$, C_{29} sterane isomerization ratios. These findings demonstrate the basin's complex hydrocarbon generation history, with biomarker distributions indicating: marine organic matter input under anoxic conditions, carbonate-evaporitic source facies and thermal equilibrium consistent with primary oil generation. The results provide valuable insights for exploration strategies in similar frontier basins, with implications for reducing exploration risk and optimizing resource development. Future studies should combine these geochemical data with structural and stratigraphic analyses to refine migration models.

Keywords: Precaspian Basin, biomarker analysis, organic geochemistry, sterane, terpane, GC-MS, source rock, depositional environment

Introduction

One of the key applications of organic geochemistry is the detailed study of the molecular composition of oil and gas. The south-eastern Precaspian Basin (Figure 1) represents a critical hydrocarbon province where understanding petroleum systems is essential for exploration and production strategies [1]. This study employs advanced organic geochemical techniques to characterize five crude oil samples from the region, focusing on biomarker analysis through gas chromatography-mass spectrometry (GC-MS). Biomarkers serve as molecular fingerprints that provide invaluable insights into hydrocarbon origin, source rock characteristics, and thermal history. Over 600 biomarkers have been identified in oils, and they are widely used to address various geochemical challenges, including the exploration and assessment of oil fields. Most common of biomarkers presented in Figure 2 (a). By examining terpane and sterane distributions, key aspects of the basin's petroleum system, including depositional environments (marine vs. lacustrine), source rock lithology (shale vs. carbonate), geological age (Paleozoic to Mesozoic), and thermal maturity were elucidated [2].

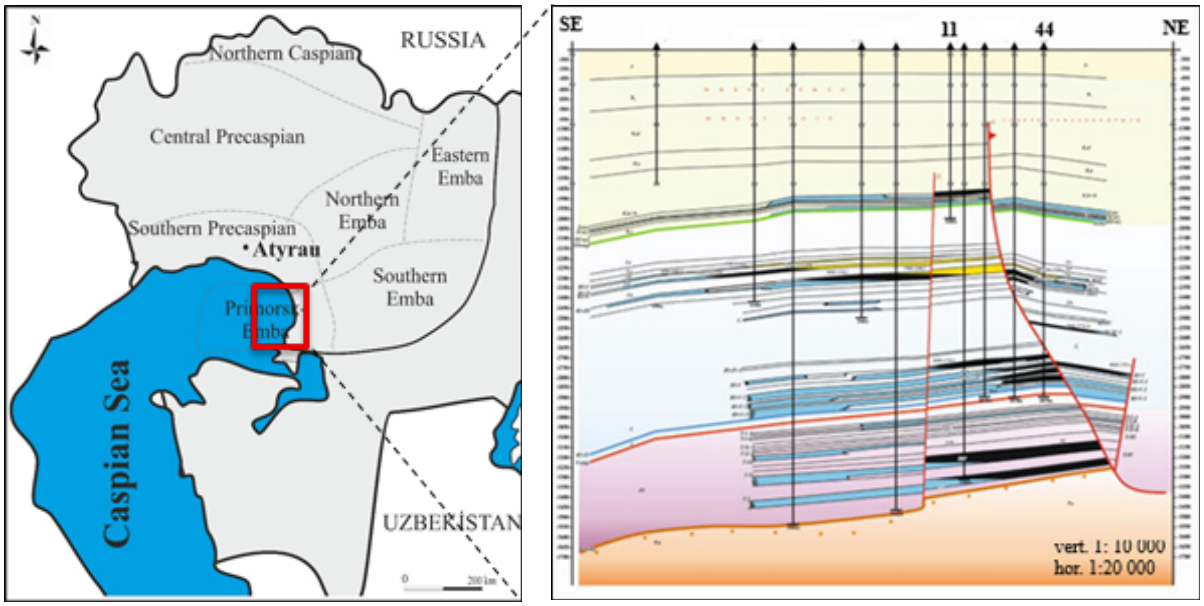

Figure 1 – Study area

Materials and methods

Five crude oil samples from the south-eastern Precaspian Basin were analyzed using gas chromatography-mass spectrometry (GC-MS) (Figure 2 (b)) to assess their biomarker composition. The oil density in analyzed samples ranges from 865 to 895 kg/m³. The oils contain 0.31–1.47% sulfur, 0.97–2.9% paraffin, 1.38–3.95% resins, and 1.7–1.96% asphaltenes. First, the oil samples were separated into saturated and aromatic fractions using solvents. Saturated hydrocarbons were extracted using n-hexane, while aromatic hydrocarbons were eluted with dichloromethane (CH_2Cl_2) as the solvent. The analytical procedure involved vaporizing the samples in a gas chromatograph equipped with a capillary column, where helium carrier gas facilitated component separation. The eluted compounds were then ionized in the mass spectrometer via electron impact, with subsequent mass-to-charge ratio separation enabling molecular identification. The resulting chromatographic data provided diagnostic insights into hydrocarbon origin, thermal maturity, and depositional history [2, 3].

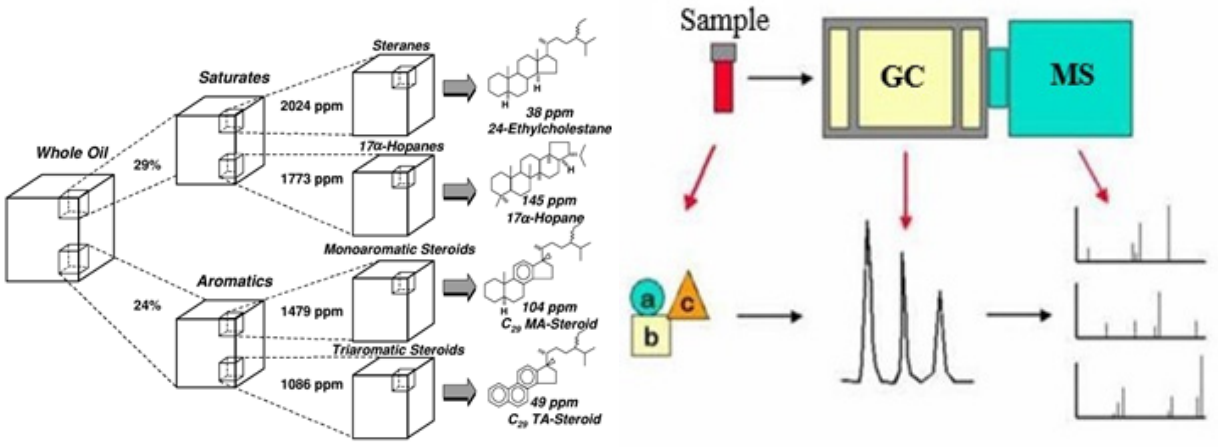

Figure 2 – (a) Composition of oil (Peters and Moldowan, 1993); (b) A simplified diagram of a GC-MS

Results and discussion

The key biomarker ratios obtained through gas chromatography-mass spectrometry (GC-MS) analysis of crude oil samples from the study area presented on Table 1.

Table 1 – GC-MS Results

Parameters	Well #				
	48	11	44	17	20
Horizon	J3	K1	J2	J2	J2
SAT/ARO ratio	0.54	0.44	1.43	1.02	1.78
C_{26}/C_{25} TT		0.59		0.79	0.75
T_s/T_m		0.46		0.92	0.95
$C_{29}T_s/ C_{29}T_m$		0.14		0.38	0.36
C_{29}/C_{30}		5.40		4.78	5.55
C27,%	36	41	35	38	38
C28,%	21	19	24	19	19
C29,%	43	40	41	43	43
C_{29} 20S/(20S+20R)	0.54	0.34	0.55	0.57	0.58
C_{29} ββ/(αα+ββ)	0.57	0.48	0.71	0.61	0.61
C_{28}/C_{29}	0.49	0.46	0.57	0.45	0.44

Biomarkers are organic molecules preserved in oil since the formation of the original organic matter. They provide critical information about the origin of hydrocarbons, the conditions under which they formed, the lithology of the source rock, and the thermal maturity of the organic material. Below, we explore how biomarkers are used to interpret the sedimentation environment, type and age of the source rock, and thermal maturity [4–6].

Sedimentation Environment

Terpanes and steranes were prioritized for environmental assessment. Terpanes comprise both tri- and pentacyclic structures, with pentacyclic terpanes (hopanes) demonstrating higher abundance in marine-derived oils relative to their tricyclic counterparts. The C_{26}/C_{25} tricyclic terpane ratio serves as a diagnostic tool for discriminating between lacustrine and marine depositional settings, where elevated ratios (>1) typically signify lacustrine origins [4, 5, 7]. In the analyzed samples, C_{26}/C_{25} ratios ranged from 0.59 to 0.79, consistent with a marine depositional environment [8]. Steranes Triagle diagram of C 27%, C 28% and C 29% steranes concerning the selected samples, showing genetically relationships of the samples that deposited under marine environment (Figure 3) [5].

Type of Source Rock

Biomarker composition provides critical insights into source rock lithology. Specifically, the C_{29}/C_{30} hopane ratio serves as a key diagnostic parameter: elevated ratios (4.78–5.55) in the studied samples indicate a carbonate-dominated source rock, while higher values would typically suggest carbonate-rich depositional environments [4, 5, 9]. Notably, oils originating from organic-rich evaporitic carbonate sequences characteristically exhibit increased C_{29} norhopane concentrations relative to C_{30} hopane, offering a distinct fingerprint for such source facies (Figure 4).

Age of Source Rock

The geological age of source rocks can be determined through C_{28}/C_{29} sterane ratios, which exhibit a progressive increase from older to younger stratigraphic units. This trend reflects the evolutionary expansion of phytoplankton communities through geological time [5, 10]. In the

analyzed samples, C_{28}/C_{29} sterane ratios of 0.44–0.57 suggest hydrocarbon generation from source rocks spanning the Paleozoic (Cretaceous-Permian).

Thermal Maturity

Thermal maturity, a critical factor in oil evaluation, can be assessed using specific biomarker ratios. The T_s/T_m ratio is a reliable indicator of both maturity and the depositional environment. A T_s/T_m ratio of less than 1 typically indicates an anoxic environment. T_s is more thermally stable than Tm, making the T_s/T_m ratio a useful parameter [5, 9, 11, 12]. In the studied samples, Ts/Tm <1 (0.46–0.92) together with $C_{29}T_s/ C_{29}T_m$ values confirm thermal maturation from peak oil window to late (Figure 5).

Two other ratios, C_{29} 20S/(20S+20R) and C_{29} ββ/(αα+ββ) sterane, are effective for determining the thermal maturity of source rocks [10]. The C_{29} 20S/(20S+20R) ratio increases from 0 to 0.55 as maturity progresses. A ratio below 0.50 indicates immature source rocks, while a ratio above 0.54 suggests mature source rocks [2, 5, 13]. Observed values of 0.34–0.58 C_{29} (20S/(20S+20R)) and 0.48–0.71 C_{29} (ββ/(αα+ββ)) consistently indicate source rocks within the principal oil generation zone (Figure 6).

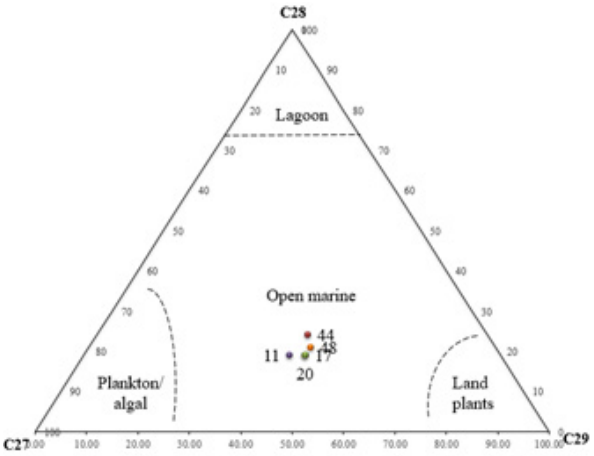

Figure 3 – Steranes tiagle diagram

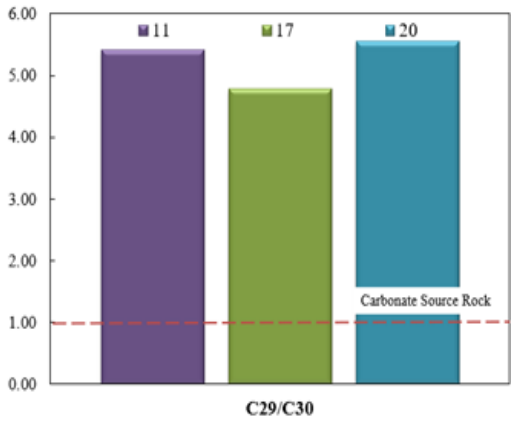

Figure 4 – Type of source rock

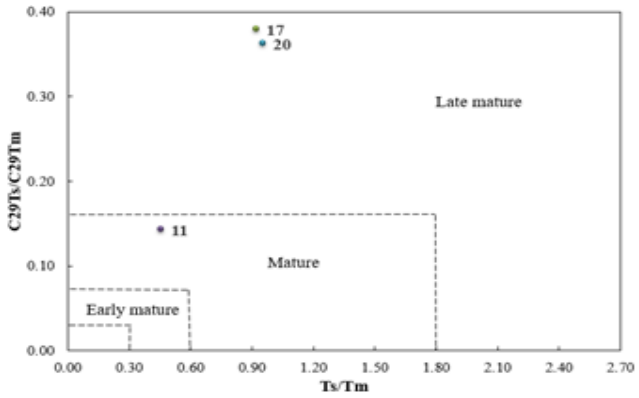

Figure 5 – Ts/Tm vs $C_{29}T_s/ C_{29}T_m$

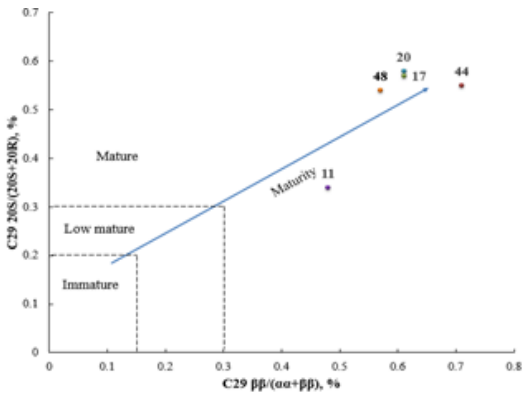

Figure 6 – Sterane isomeration

Conclusion

Organic geochemistry plays a vital role in understanding the formation, composition, and transformation of organic matter in the Earth's geospheres. Biomarkers, which are organic molecules preserved in oil, serve as powerful tools for this purpose. This comprehensive biomarker study of crude oils from the south-eastern Precaspian Basin has provided significant insights into the region's petroleum system. Through advanced GC-MS analysis of terpanes and steranes, we have established:

- Carbonate-dominated source rocks were identified as the primary hydrocarbon generators, indicated by characteristic C_{29}/C_{30} hopane ratios (4.78–5.55) and elevated C_{29} norhopane concentrations.
- Sourcing from Paleozoic (particularly Permo-Carboniferous) strata was confirmed through C_{28}/C_{29} sterane ratios (0.44–0.57), reflecting the basin's complex depositional history.
- Thermal maturity parameters Ts/Tm, $C_{29}T_s/ C_{29}T_m$ and C_{29} sterane isomerization ratios consistently placed the samples within the peak oil generation window and late maturity.

The methodology and findings presented here can be applied to other frontier basins to reduce exploration risk and optimize resource development. Future work should integrate these geochemical data with regional seismic and well-log interpretations to further constrain hydrocarbon migration pathways and accumulation patterns.

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КАСПИЙ МАҢЫ ОЙПАТЫНЫҢ ОҢТҮСТІК-ШЫҒЫС БӨЛІГІНДЕГІ МҰНАЙДЫҢ ШЫҒУ ТЕГІ МЕН ЖЕТІЛГЕНДІГІНІҢ КӨРСЕТКІШІ РЕТІНДЕГІ МҰНАЙ БИОМАРКЕРЛЕРІ

Аңдатпа

Бұл зерттеуде газ хроматография-масс-спектрометрия (ГХ-МС) әдісін қолдану арқылы Оңтүстік-Шығыс Каспий маңы ойпатының мұнай шығу тегін бес мұнай үлгісіндегі биомаркерлерді талдау негізінде зерттеу жүргізілді. Биомаркерлер көмірсутектердің шығу тегін, аналық жыныстардың сипаттамаларын және олардың термиялық тарихын анықтауға мүмкіндік беретін молекулалық көрсеткіштер ретінде қызмет етеді. Зерттелген үлгілер мынадай нәтижелер көрсетті: теңіздік шөгінді орта (C_{26}/C_{25} терпан қатынасы = 0.59–0.79), карбонатты аналық жыныстардың басымдылығы (C_{29}/C_{30} гопан қатынасы = 4.78–5.55), Палеозой (Карбон–Пермь) жыныстарынан алынған мұнай (C_{28}/C_{29} стеран қатынасы = 0.44–0.57). Ts/Tm, C_{29}Ts/C_{29}Tm және C_{29} стеран изомеризациясы сияқты қатынастар мұнайдың қалыптасу аймағы мен оның жоғары жетілу деңгейін көрсетеді. Алынған нәтижелер ойпаттағы көмірсутектердің түзілу тарихының күрделілігін айғақтайды. Биомаркерлердің таралуы аноксиялық жағдайда теңіздік органикалық заттардың қосылғанын, көмірқышқыл-эвапориттік аналық жыныстар фацияларының бар екенін және негізгі мұнай түзілу кезеңіндегі термиялық тепе-теңдік жағдайын айғақтайды. Бұл нәтижелер ұқсас шекаралық ойпаттарда барлау стратегияларын әзірлеу үшін құнды ақпарат ұсынады, тәуекелдерді азайтуға және ресурстарды тиімді игеруге мүмкіндік береді. Болашақ зерттеулерде осы геохимиялық деректерді құрылымдық және стратиграфиялық талдаулармен біріктіру арқылы мұнай миграциясы модельдерін нақтылау ұсынылады.

Тірек сөздер: Каспий маңы ойпаты, биомаркерлер талдауы, органикалық геохимия, стерандар, терпандар, ГХ-МС, аналық жыныс, шөгінді орта

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НЕФТЯНЫЕ БИОМАРКЕРЫ КАК ИНДИКАТОРЫ ПРОИСХОЖДЕНИЯ И СТЕПЕНИ ЗРЕЛОСТИ НЕФТИ В ЮГО-ВОСТОЧНОЙ ЧАСТИ ПРИКАСПИЙСКОЙ ВПАДИНЫ

Аннотация

В данном исследовании изучается происхождение нефти юго-восточной части Прикаспийской впадины с помощью анализа биомаркеров пяти проб сырой нефти методом газовой хроматографии-масс-спектрометрии (ГХ-МС). Биомаркеры выступают в роли молекулярных отпечатков, позволяющих определить происхождение углеводородов, характеристики материнских пород и термическую историю. Анализ проб выявил: морские условия осадконакопления (соотношение C_{26}/C_{25} терпанов = 0.59–0.79), преобладание

карбонатных материнских пород (соотношение C_{29}/C_{30} гопанов = 4.78-5.55), смешанное происхождение из отложений палеозоя (Карбон-Пермь) (соотношение C_{28}/C_{29} стеранов = 0.44-0.57) и по соотношениям Ts/Tm, C_{29}Ts/ C_{29}Tm и изомеризации C_{29} стеранов пиковую и позднюю зону нефтеобразования. Полученные данные демонстрируют сложную историю генерации углеводородов в бассейне, при этом распределение биомаркеров указывает на поступление морского органического вещества в аноксидных условиях, карбонатно-эвапоритовые фации материнских пород и термическое равновесие, соответствующее основной фазе нефтеобразования. Результаты представляют ценные данные для разработки стратегий разведки в аналогичных бассейнах, позволяя снижать риски и оптимизировать освоение ресурсов. Дальнейшие исследования должны объединить эти геохимические данные со структурным и стратиграфическим анализами для уточнения моделей миграции.

Ключевые слова: Прикаспийская впадина, анализ биомаркеров, органическая геохимия, стераны, терпаны, ГХ-МС, материнская порода, обстановка осадконакопления.

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