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Organic Geochemistry and Stable Carbon Isotopes of Oil Seepages in the Abu-Jir Fault Zone at Al-Anbar Governorate, Iraq

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Abstract

Oil seep samples along Abu-Jir Fault Zone were studied to determine their chemical characterization and origin. They are dominated by the normal alkanes, more complex mixture of branched and cyclic hydrocarbons. Organofacies coupled with the stable carbon isotopes have been integrated to infer the oil seep origin. Oil seeps contain H_2S gas, which derives as a catabolic by product of sulfate-reducing bacteria from gypsum of the Fatha Formation during the early diagenetic under anoxic conditions which is demonstrated by values of C29/H that are greater than 1. The oil seeps are characterized by $\delta^{13}C$ values vary from -29.0 to -27.96‰ and from -28.34 to -27.88‰ in the saturated and aromatic compounds, respectively; consequently, they have low values of the canonical variable ranged from -3.47 to -0.17 reflecting a marine non-waxy oil generated from planktonic kerogen of type-II that has been partially mixed with the terrestrial origin. The values of the tricyclic terpanes (C22/C21 and C31R/H) that are higher than 0.5 and 0.25 respectively support the marine source rocks. The Triassic age was suggested for the oil age in the dependence of the occurrence of the aromatic dinosteranes which marked dinoflagellates were participated in the oil derivation.

Keywords: Organic geochemistry, Carbon isotopes, Biodegradation, Oil seep, Canonical variable.

الجيوكيمياء العضوية ونظائر الكاربون المستقره للنضوحات النفطية في نطاق فالق ابو الجير محافظة الانبار، العراق

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الخلاصة

تمت دراسة عينات من النضوحات النفطية المنتشرة على طول نطاق فالق ابو الجير لتحديد المواصفات الكيميائية والاصل لهذه النضوحات، يتالف التركيب الكيميائي بصورة رئيسية من الالكانات بالاضافة الى خليط معقد من الهيدروكربونات المعقدة والحلقية . السحن العضوية ونظائر الكاربون المستقر تمت دراستها بصورة متكاملة ومتزامنة لتحديد اصل هذه النضوحات، تحتوي النضوحات النفطية على غاز كبريتيد الهيدروجين والذي يعد كناتج لعمليات الاختزال التي تتم بواسطة البكتريا على الجبس المترسب ضمن تكوين الفتحة خلال المرحلة المبكرة للعمليات التحويرية تحت ظروف اختزالية والذي انعكس على قيمة C29/H التي تكون اكبر من واحد وتعطي مؤشر على البيئة الاختزالية ، قيم نظائر الكاربون المستقرة للنضوحات النفطية تتراوح من – 29 الى – 27.97 ‰ للمركبات المشبعة ومن – 28.34 الى – 27.88 ‰ للمركبات الاروماتية ، في حين تبلغ قيمة متغير الكانونيكل من – 3.47 الى – 0.17 مما يعكس نفوط غير شمعية

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متولدة في بيئة بحرية من نوع كيروجين 2 العائد الى الكائنات الدقيقة العالقة ذات الاصل البحري والتي تكون ممتزجة جزئيا مع النباتات ذات الاصل القاري . ان نسب التربين ثلاثي الحلقات (C22/C21 ، C31R/H) تكون اعلى من 0,5 و 0,25 على التوالي مما يعطي دليلا على ان الصخورالمصدرية المولدة للنفط تكون ذات اصل بحري ، ان عمر الصخور المولدة للنفط يقدر بالعصر الترياسي بالاعتماد على تواجد السترين الاروماتي ضمن العينات والذي يعود اصله الى الطحلبيات المتكيسة ذات الاسواط.

Introduction

Many oil seeps can be seen on the surface in the different locations in Iraq which are related with geology and structure. The Abu-Jir Fault Zone (AJFZ) is of the greatest factors influencing the rise in oil to the surface. The study area is located within the Abu-Jir Fault Zone (AJFZ) Figure-1. Accordingly, set of springs emerged to the surface**.** The AJFZ is a fault basin provides many oil seepages to the surface [1], [2] and [3]. The location of theses seepages is clearly tectonically controlled [4]. The hydrocarbon is represented by heavy crude oil, bitumen, asphalt and dissolved H_2S gas that accompanies the spring water flowing on the surface**.** Hydrocarbon seep has been continual since the Miocene so far. Seep activity begun in the Middle Miocene and much of oil expelled from the Jurassic and Lower Cretaceous source rocks [4]. The geology of the study area is characterized by the many exposures of the Upper member of Euphrates Formation (Early Miocene) which mainly consists of limestone, marl and dolomitic limestone Figure-1. The Nfayel beds (Lower Miocene) conformable overlays the Euphrates Formation consisting of green marl, limestone and gypsum. These beds together with the Fatha Formation (Middle Miocene) exposed on the surface, forming a semi flat landscape characterizes by scattered small hills. The Injana Formation that composed of clasitic has scarcity outcrops in the study area. The main structure in the study area is AJFZ in which, water springs and oil seepage flow. H_2S gas, volatile materials and Bitumen associated oil seeps intrude limestone, marl and gypsum ascending upwards to the surface where H_2S and volitiles escape to the atmosphere leaving behind the bitumen. The previous studies that have been carried on the study area focused on the spring water, and did not interest with the water-associating hydrocarbon. Hydrogeochemical studies throughout the AJFZ demonstrated that the spring water is a marine origin composed from mixture of oil field and meteoric waters [1], [2] and [3]. Alkans, polycyclic alphatics and polycyclic aromatic hydrocarbons can be used for describing the characterization of oil source [5]. Carbon isotopes provide information on the generation, maturation and genetic correlation of hydrocarbons and precursors which can be used in oil and gas exploration [6]. The hydrocarbon source can be defined by using the distribution of n-alkanes, $\delta^{13}C$ and $\delta^{34}S$ in crude oils [7]. This paper deals with the organic geochemistry of saturated and aromatic compounds for seven oil seepages in the study area to describe the organofacies and define the origin of oil seeps.

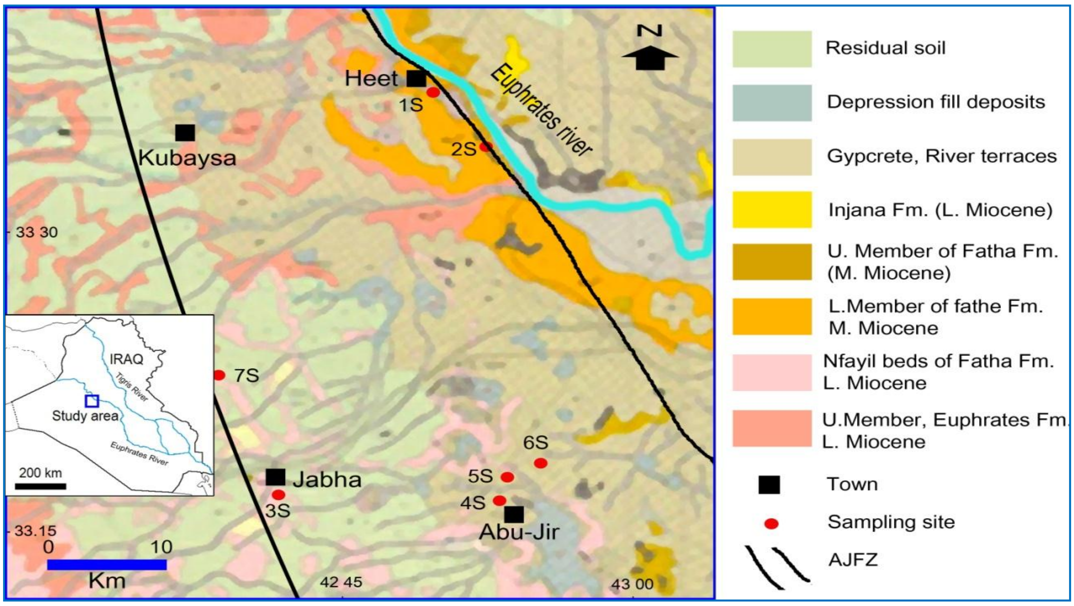

Figure 1- Geological map of the study area shows the sampling site of oil seeps within the Abu-Jir Fault Zone (AJFZ), The AJFZ is installed in this map based on [1] Modified after [8]

Materials and Methods

Seven samples of oil seeps were collected from area restricted between Heet and Abu-Jir village as shown in Figure-1. Gas chromatography-mass spectrometry (GC-MS) was used for analyzing oil seep samples and as a key technique for the interpretation of the organic geochemistry of the oil constituents. All analyses used in this paper have been done in the Geomark Research, Inc. USA. Carbon isotope ratios are reported as $\delta^{13}C$ and expressed as:

$$\delta^{13}C= [\{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}\} / (^{13}C/^{12}C)_{standard}]\ 1000\ (‰)$$

A Cretaceous marine organism named Peedee belemnite (PDB) whose shell consists of $CaCO_3$ was used as a standard for the measurements of C isotope. The seep oil samples were fractionated using high performance liquid chromatography (HPLC) into saturates, aromatics, and resins following the standard procedures outlined by [9] The canonical variable relationship (CV) was used to distinguish oils derived from marine and non-marine sources using equation postulated by [10]:

$$CV= -2.53\ \delta^{13}C_{sat.} + 2.22\ \delta^{13}C_{arom.} - 11.65.$$

Results (Biodegradation):

A redox gradations as oxic–suboxic–anoxic and euxinic postulated by [11] is presented in Table-1.The studied oil samples are represented by wide range of redox potential (Eh). They were migrated from oil reservoir of euxinic conditions. Then these conditions have been sequentially changed during ascended upward from euxinic, suboxic near the surface to oxic on the surface due to the intraction with the atmosphere. Under oxic conditions, aerobic micro-organism consumes oxygen for metabolism, causing suboxic conditions. In case of oxygen depletion, the organic matter has broken down by other available oxidants such as Fe-Mn oxides and sulfates. In the studied area, sulfate of Fatha Formation represented by gypsum is an oxidant agent. As the condition becomes anoxic due to the depletion of oxygen, H_2S gas associated oil seeps derived as a catabolic by product of sulfate-reducing bacteria. Methanogenic bacteria begin to break down organic matter [12]. *Desulfovibrio desulfuricans* is a sulfate-reducing bacteria [13] reduces (SO_4^{-2}) to H_2S to get energy during anaerobic respiration [14] In the study area, bacteria under euxinic conditions reduce sulfate in gypsum forming sulfur deposits and releasing Ca ions to the spring water and H_2S gas to the atmosphere. The H_2S gas escape to the atmosphere leaves behind bitumen-rich oil behind. It is known, the microbial activity near surface being effective. In a sense, oxygen after intensive biodegradation approached to zero [11].

Table 1- Redox classification of the depositional environments, after [11]

Redox classes	Oxic	Suboxic	Anoxic	Euxinic
			No free H_2S in the water column	Free H_2S present in the water column
O_2 concentration in bottom waters (ml O_2/l H_2O)	$[O_2]>2$	$2>[O_2]>0.2$	$[O_2]<0.2$	$[O_2]=0$

Organofacies:

Organofacies are characterized certain biotic sources and retain their source information after burial in sediments [15]. Stable carbon isotope composition and biomarker properties of oil seeps are listed in Table-2. The percentages of Aromatic, Saturated, NOS and Asphalt presented in Table-2 are illustrated in Figure-2. Asphalt is dominant in all samples except sample no. 4 which is characterized by the dominance of Aromatic compounds. The high quantity (91.6%) of Asphalt in the sample no. 5 reflects low pressure, in a sense, the longtime exposure to the atmosphere, where aromatic and saturated have been released. This conclusion is supported by strong negative correlations between asphalt and both of aromatic and saturated compounds Figure-3. NOS% is positively correlated with both aromatic and saturated compounds; the coefficient of determination (R^2) was computed to be 0.855 and 0.713 and defined by the exponential equations: $Y=1.355e^{0.35x}$ and $Y=1.098e^{0.83x}$ respectively Figure-3. The isoprenoids (terpenoids) which are diverse organic class were diagnosed in the studied samples Figure 4. Aryl isoprenoids were formed due to the diagenetic transformation of Aromatic carotenoids. These compounds exist in the C10–C31 range [16] and [17] the predominance of *n*-alkanes and acyclic isoprenoids in the C11 to C35 region of the gas chromatograms is diagnostic of marine organofacies sources [18]. The relatively enriched $\delta^{13}C$ signatures in the studied samples confirm that the origin of aryl isoprenoids was derived from Chlorobiaceae which is green sulfur bacteria common in the anoxic zone can perform anoxygenic photosynthesis in existence of H_2S-saturated waters [19]. Hartgers [20], [21] and [22] stated that the origin of aryl isoprenoids from

Chlorobiaceae can be confirmed by their relatively enriched $\delta^{13}C$ signatures. The relative differences among the peaks of the Aryl isoprenoids in the studied samples in Figure-4 are attributed to the hydrocarbon fractionation during biodegradation which relies on the timing of seepage. Dinosteranes were identified in the all samples and documented in Figure-5 to express as mark for the dinoflagellates. [23] Stated that the Dinosteranes are used as a mark for the dinoflagellates that were originally considered existing only in Triassic and younger age. The values less than 1.0 of the steranes ratio (C28/C29) in all samples indicate an oil of marine origin generated from source rock older than Jurassic and Cretaceous rocks [24]. A crystalline hydrocarbon, phenanthrenes ($C_{14}H_{10}$) was diagnosed in the studied samples Figure-6. A negative correlated was found between the phenanthrenes and quantity of asphalt. Dibenzothiophene (DBT) is a model compound among sulfur-containing Hydrocarbon aromatic compounds in crude oil [25]. Under low oxygen conditions, DBT degradation has little knowledge despite of a various bacteria can aerobically degrade it [26]. The highest peaks were noticed in sample no. 4 which contains a high quantity of aromatic (37.8%) and saturated (10.5%) compounds, whilst the lowest pecks were in sample no 5 which contains a high quantity of asphalt Figure-7. Depending on the values of C_{27}, C_{28} and C_{29}, Oil samples were plotted on the ternary diagram designed by [27]. They occupied the field of bay and estuarine (Figure 8), except for one sample (No. 5S) fell in the terrestrial field. It looks like of terrestrial origin has less reducing conditions and receiving significant clastic input [28]. It is believed that this sample subjected to severe weathering and biodegradation due to the long exposure to the atmosphere; and therefore, it has the same origin of the other samples, doesn't typical terrestrial origin. In all studied samples, values of C22/C21 are higher than 0.5 and C31R/H are greater than 0.25 (Table 2); if the value of C22/C21> 0.5 and C31R/H > 0.25 in all studied samples indicates marine source rocks [29]. It is evident that the conditions were anoxic due to the values of C29/H, where they are greater than 1.0 in all samples (Table2). Peters et al [30] stated a greater than 1.0 of this parameter indicates oil generated under anoxic carbonate or marl source rocks. Gammacerane index (Ga/C31R) is evident for the salinity of the depositional environment; if it is lower than 0.5 it means a low salinity [29] Three oil seep samples have less than 0.5 of Ga/C31R value, but the other four samples are a little higher than 0.5 (Table-2) indicating low to high water salinity. Oleanane in crude oils were used as a marker for both source input and geologic age; the angiosperms are present in Late Cretaceous; the absence of Oleanane in Early Cretaceous and older sediments is known [24] The value 0.0 of Oleanane in all oil seep samples Table-2 indicates either that this Oleanane does not contribute in enriching the source rock, or the age of oil is older than the beginning of the emergence of these plants (Late Cretaceous). The non-condensate samples indicate a non-gas field origin based on low saturated/aromatic hydrocarbon ratio (0.21, 0.3, 0.26, 0.28, 0.26, 0.2 and 0.34). The condensate samples of high saturated/aromatic hydrocarbon ratio (greater than 10) indicate gas fields [31].

Stable Carbon Isotopic Composition:

Stable carbon isotope data of the saturate and aromatic hydrocarbons are listed in Table-2. In the purpose to differentiate algal from land plant source materials and marine from continental depositional environments, the stable carbon isotopic composition of organic matter was recommended [15] and [32]. The saturated and aromatic fractions of the oil seeps in the study area have a $\delta^{13}C$ values vary from -29.0 to -27.96‰ and from -28.34 to -27.88‰ respectively. They are within the $\delta^{13}C$ range value (34‰ to -18‰) that characterizes the most of crude oil [6]. Stable carbon isotope values of oils are dependent mainly on the depositional environment of the source rock and the degree of thermal maturity at which the oil was expelled. The decreasing contribution of terrestrial organic matter to the marine sediments is reflected in the carbon isotope composition [33] and the carbon isotope ratio reflects the carbon source [34]. Consequently, the low values of CV in the study samples reflect a less contribution of terrestrial organic matter. The canonical variable (CV) values range between -3.47 and -2.66; as it is lower than 0.47 indicating typical marine (non-waxy) oils Figure-9 where [10] distinguished oils derived from marine and non-marine sources from different parts of the world using the CV value. The $\delta^{13}C$ values of crude oil are lower than those of the organic matter from which they should derive, but they are similar to the ratios of the lipid fractions, especially of lower plants and animals [35]. It is noteworthy that the isotopic fractionation relies on time and type of processes. Maturation, migration, bacterial activities and pore water participated in the isotopic fractionation. During the maturation, the simple molecules rich in H and ^{12}C changes to the complex molecules of less H and ^{12}C. The heavy carbon (^{13}C) enriched in the aromatic fraction during oil migration, whilst depleted in the saturated fraction [33]. Bacterial methanogenesis maybe played a complex role and produced a bacterial methane very ^{12}C-rich due to the sulfate reduction in the anaerobic bitumen-rich sediments leaving behind a residual pore water with significantly enriched in ^{13}C. Oil before seeping in the study area has been mixed with groundwater; pore waters have ^{13}C/^{12}C ratios no lower than organic matter [33]. Type-I oil generally has heavier isotope values than type-II oil, which matches the source rock. Stable carbon isotope data of the saturate and aromatic hydrocarbons are plotted in Figure-9. The stable carbon isotope composition shows type-II oils belong to the planktonic kerogen. Oil seep samples were isotopically plotted and compared with the global crude oil samples (Figure-10). Hence, the studied samples looks like to be derived from Eocene source rocks based on similar isotopic composition with other proposed Eocene oils in California and based on oil-source rock correlation studies according to [36] and [31]. It is believed that the source rocks have an older age than the Eocene. This anomaly suggests a considerate either that the oil had matured in the Eocene, or may attribute to the isotopic fractionation during diagenesis, in particular, isotopically crude oil is lighter than kerogen from which they were generated. The δ^{13}C in kerogen is mainly varied from -33 to -17‰ [37].

Table 2- Stable carbon isotope composition and biomarker properties of oil seeps from AJFZ

Parameters		Sample numbers						
		1S Heet spring	2S Gypsum bitumeous	3S Jabha sprin	4S Abu jer water	5S Ash	6S Abu-jir	7S Awasel
GC-MS Saturated hydrocarbons	Ts/(Ts=Tm)	0.10	0.12	0.11	0.11	0.13	0.12	0.11
	Oleanane Index %	0	0	0	0	0	0	0
	Gammacerane Index %	0.49	0.91	0.43	0.49	0.56	0.53	0.52
	C35/C34 Homohopane	1.01	1.18	1.03	0.92	0.94	1.09	0.95
Regular Steranes and Sterane ratio	C27 (%)	33.6	28.1	34.7	35.4	13.1	29.8	32.7
	C28 (%)	23.5	23.1	21.4	21.4	20.1	23.6	21.5
	C29 (%)	42.8	48.8	43.9	43.2	66.9	46.6	45.8
	C28/C29 <1= marine	0.55	0.47	0.49	0.49	0.3	0.5	0.47
	Diasterane Index	0.85	0.23	0.67	0.56	0.90	0.40	0.60
Stable C isotopes	δ^{13}C saturate (‰ PDB)	-28.23	-28.50	-28.18	-27.96	-29.0	-28.44	-28.20
	δ^{13}C aromatic (‰ PDB)	-28.22	-28.26	-28.22	-28.18	-27.88	-28.34	-28.09
	δ^{13}C whole oil (‰ PDB)							
	CV	-2.88	-2.28	-3.00	-3.47	-0.17	-2.61	-2.66
Bulk constituents	Sat%	6.8	5	7.9	10.5	1.2	6.6	6.5
	Aro%	32.4	16.8	30.6	37.8	1.9	33.2	18.8
	NSO%	26.8	18.8	18.6	22.8	5.4	25.6	17
	Asphalt%	33.9	59.4	42.8	28.9	91.6	34.6	57.7
	Sat/Aro%	0.21	0.3	0.26	0.28	0.62	0.2	0.34
	Paraffin/Naphthene	0.64	1.24	1.18	1.04	0.73	1.14	0.38
Tricyclic Terpane	C22/C21>0.5 marine	0.99	1.02	1.0	1.07	1.54	0.99	1.07
	C24/C23	0.27	0.25	0.26	0.25	0.4	0.27	0.27
Norhopane/Hopane	C31R/H if> 0.25 marine	0.28	0.3	0.29	0.26	0.29	0.29	0.26
	C29/H if >1 anoxic, and thermal mature	0.98	1.18	1.06	1.06	1.02	1.2	1.05
Gammacerane index	Ga/C31R < 0.5 L. salinity	0.49	0.91	0.43	0.49	0.56	0.53	0.52
Oleanane index	OL/H >0.2= younger than Cret <0.2=L. Cret. If 0.0= Earler than Cret.	0.0	0.0	0.0	0.0	0.0	0.0	0.0

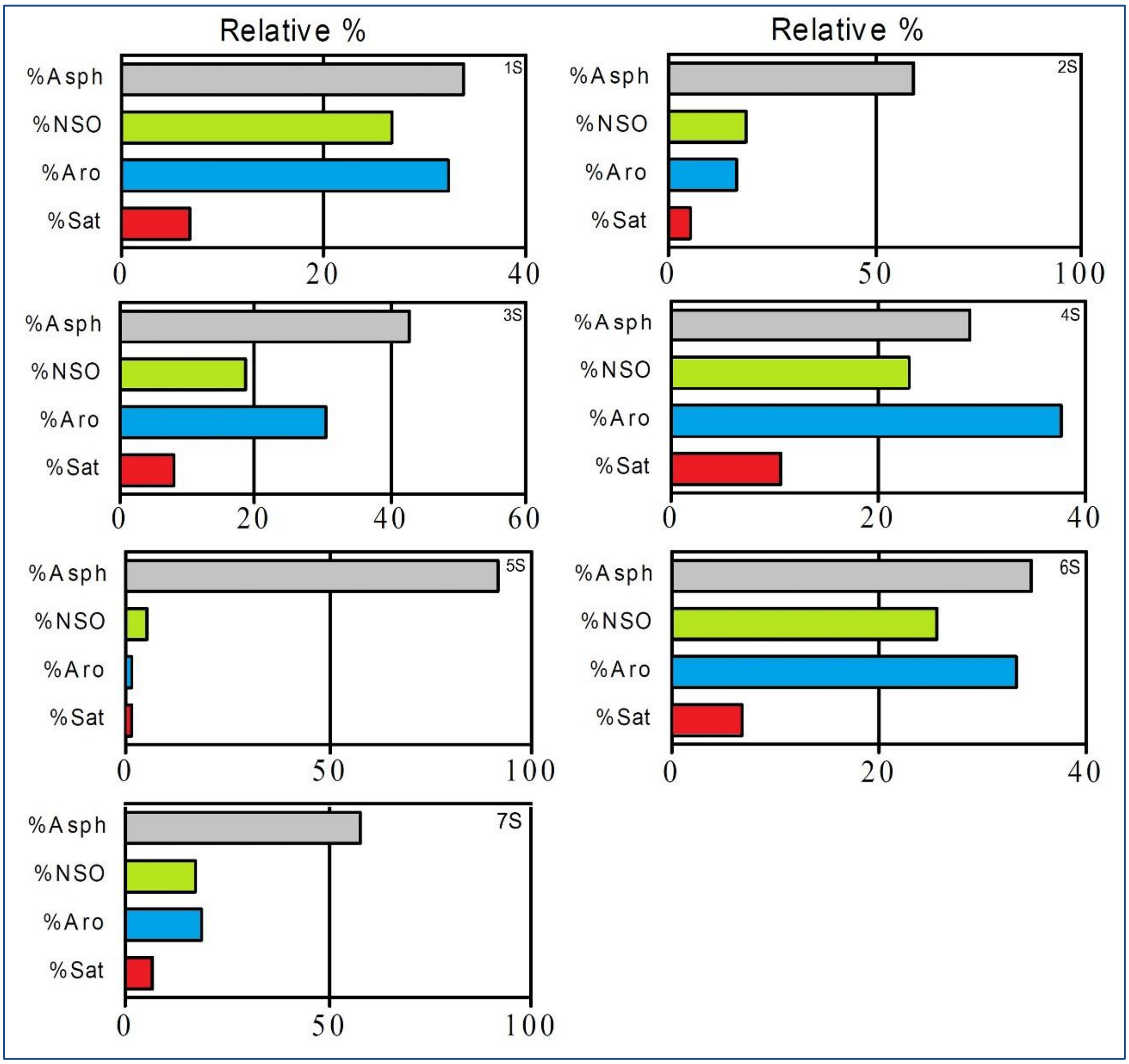

Figure 2- Whole organic compounds in the studied oil seeps; symbols (1S to 7S) refer to sample numbers.

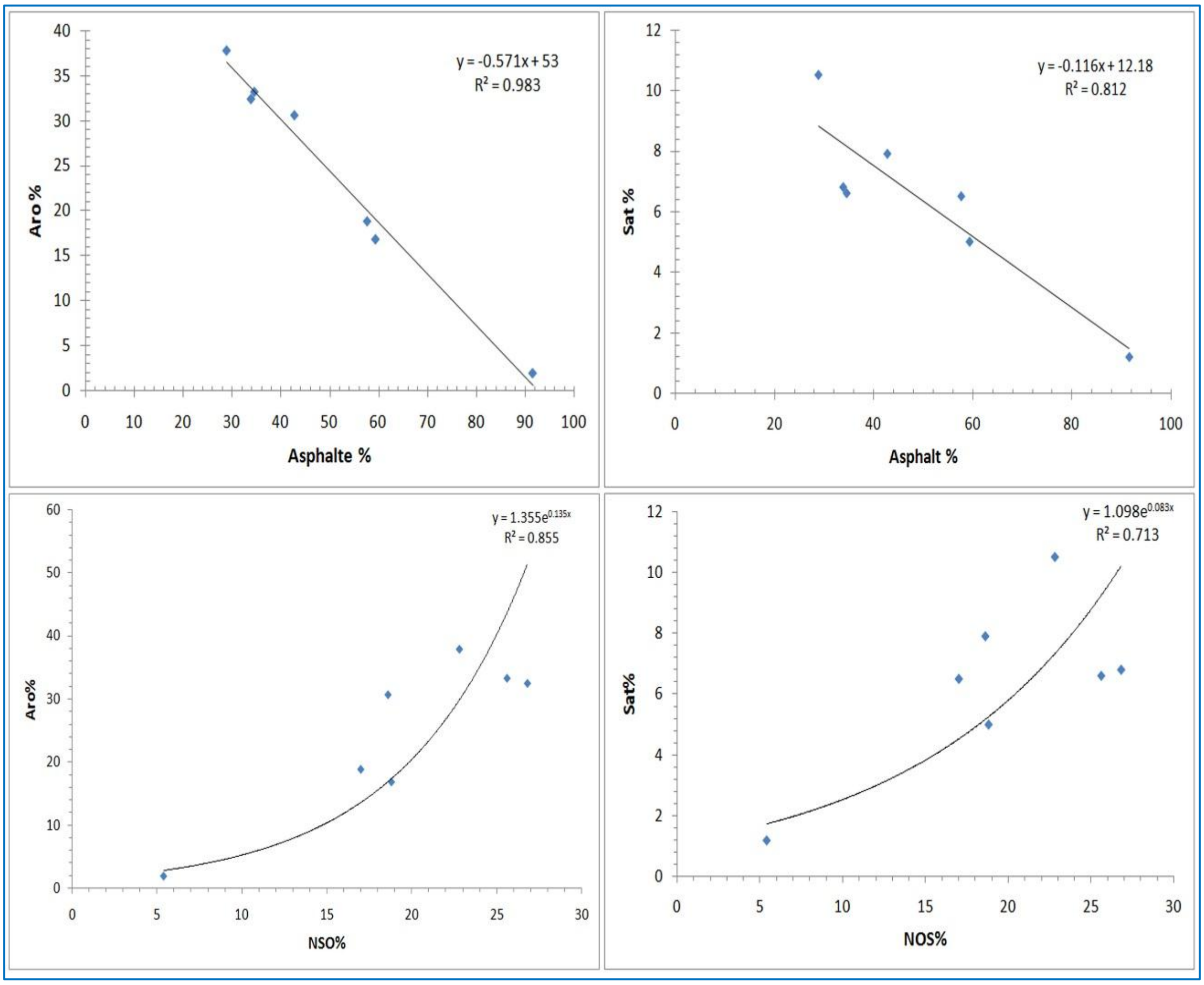

Figure 3- Relationships between organic compounds in the oil seeps.

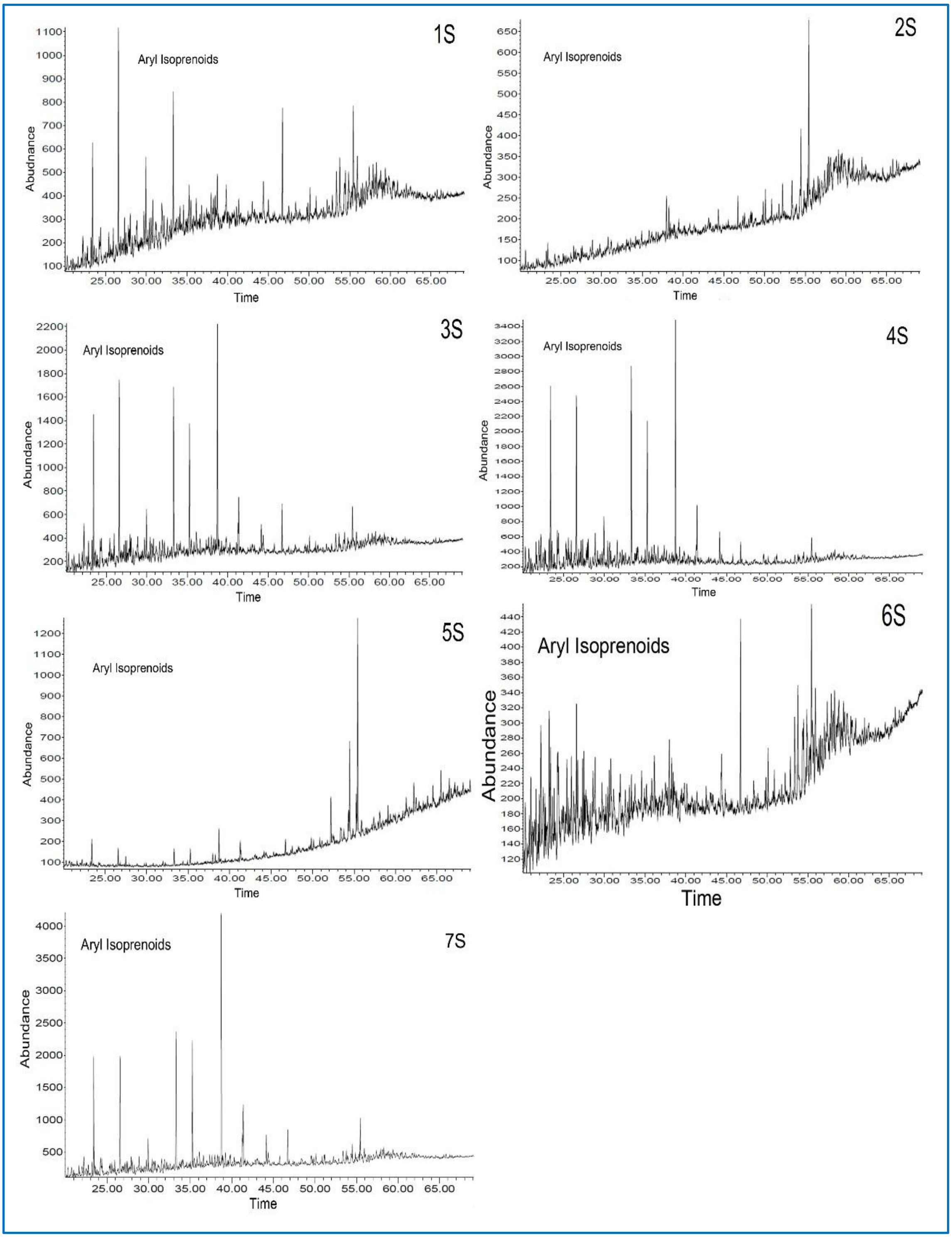

Figure 4- Aryl isoprenoids in the studied oil seeps; symbols (1S to 7S) refer to sample numbers.

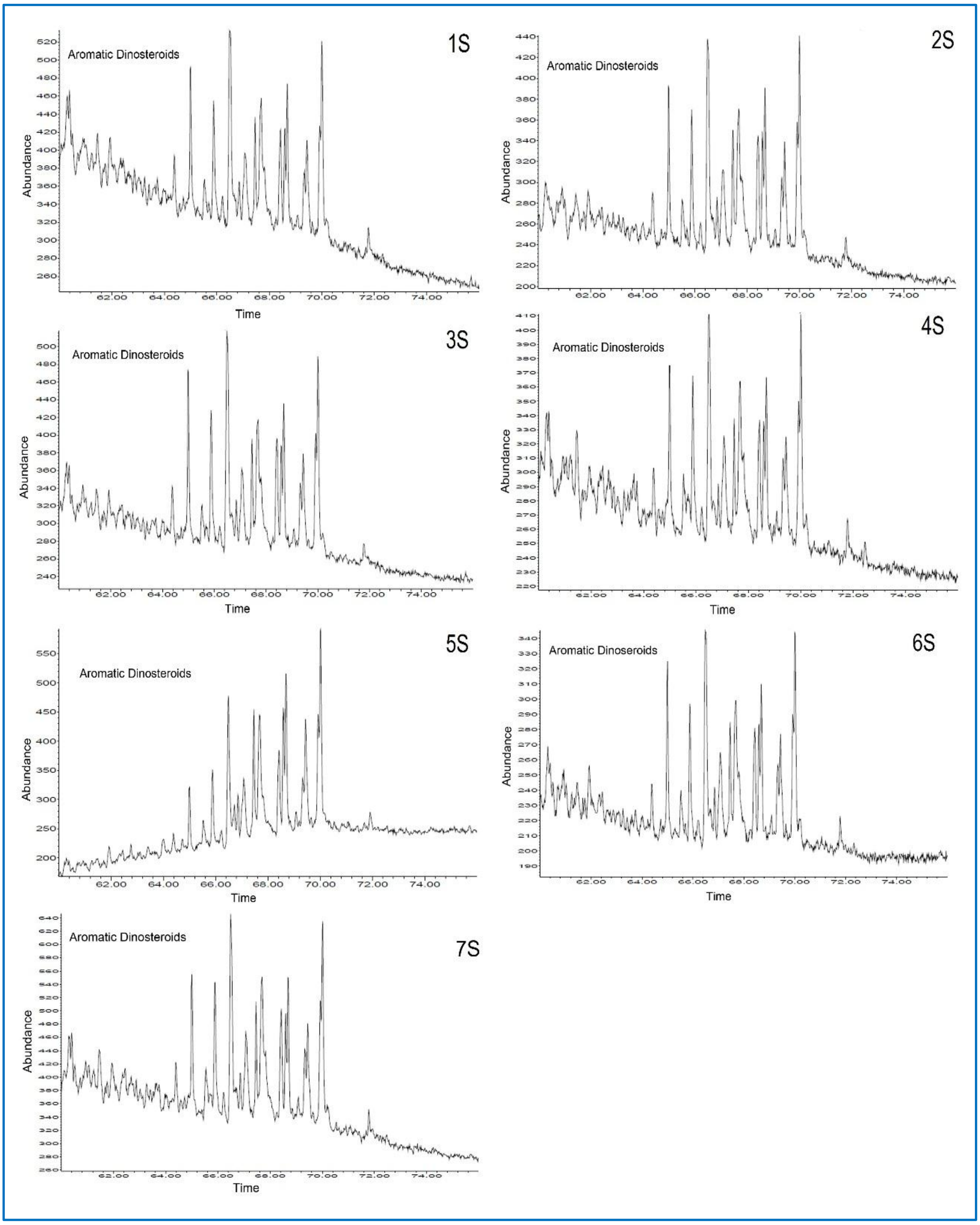

Figure 5- Aromatic dinosteranes in the studied oil samples; symbols (1S to 7S) refer to sample numbers.

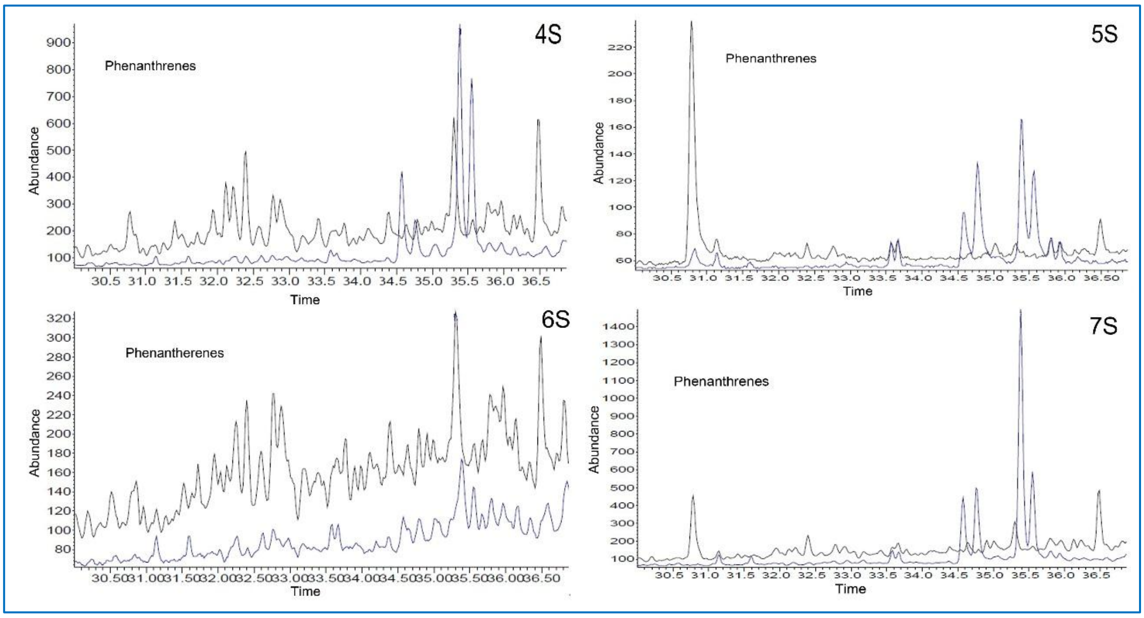

Figure 6- Phenanthrenes in the studied oil seeps samples (4S, 5S, 6S and 7S).

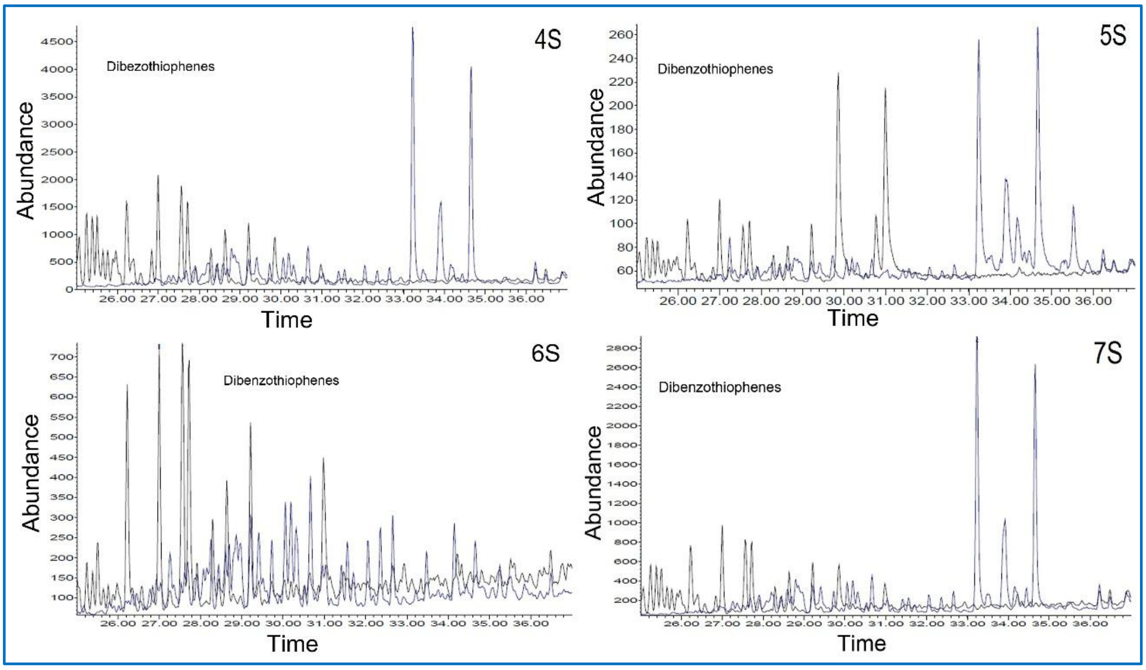

Figure 7- Dibenzothiophene in the studied oil samples (4S, 5S, 6S and 7S).

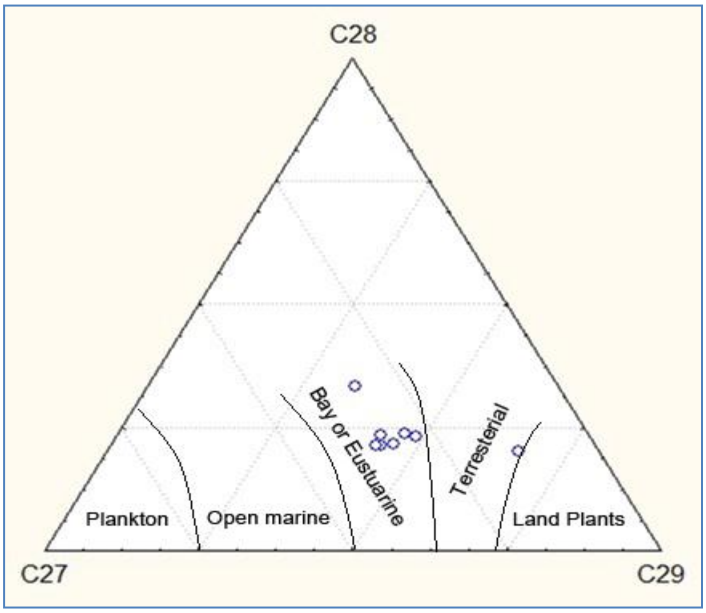

Figure 8- Ternary of regular steranes (C_{27}, C_{28} and C_{29}) shows organic facies of the oil seeps in the study area; diagram after [27].

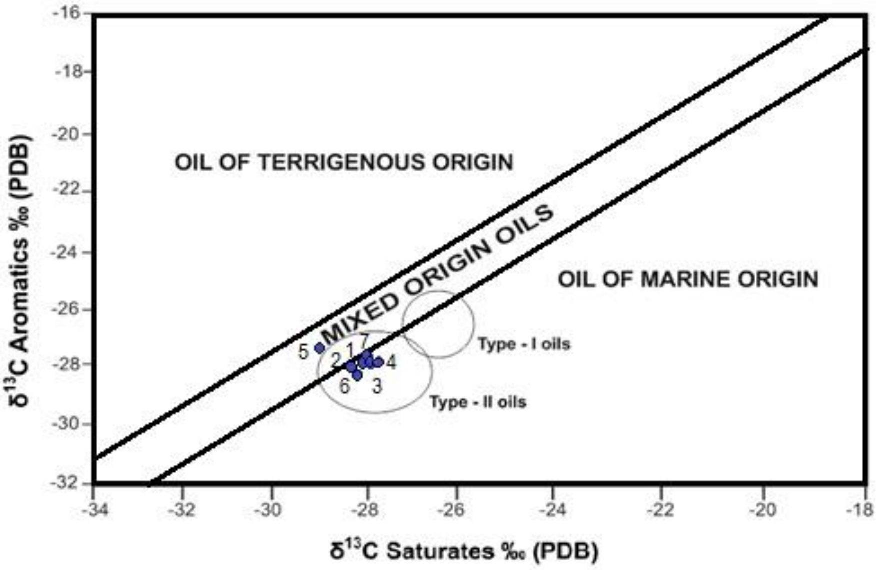

Figure 9- Relationship between the carbon stable isotopic composition of the saturate and aromatic fractions for seep oils from the AJFZ diagram after [10].

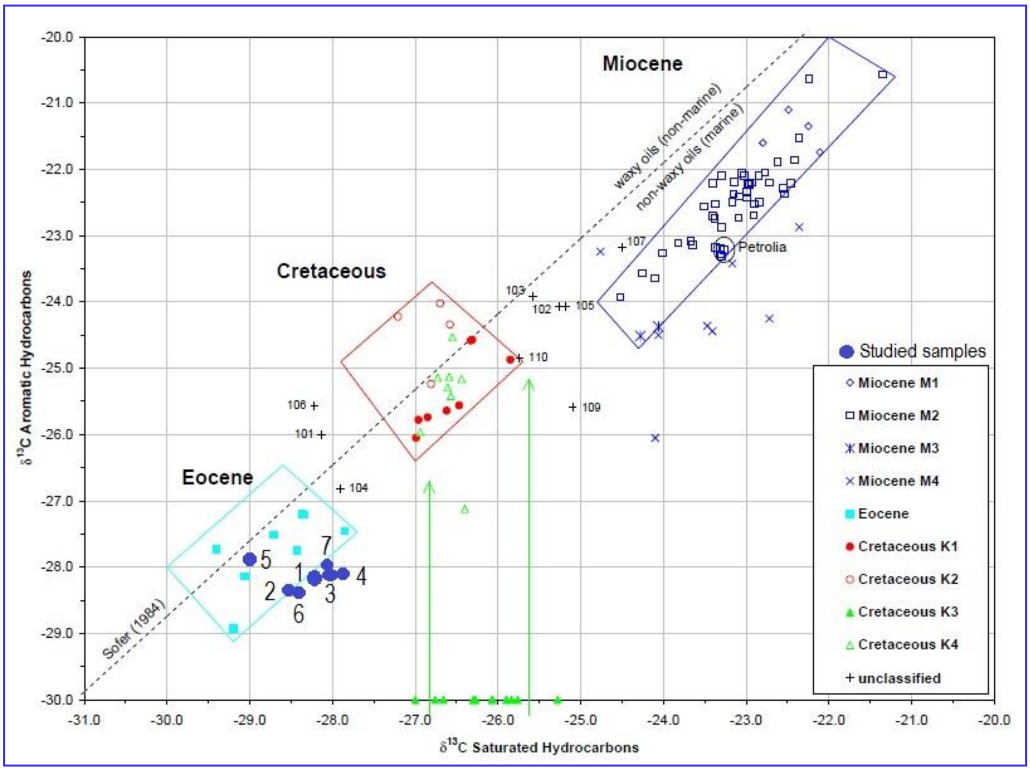

Figure 10- Isotopic composition oil seeps compared with the results of [38] oils, oil seeps, and oil stains, northern California, diagram after [10].

Conclusions:

Based on this study, it is possible to conclude these points:

1. The gypsum of Fatha Formation was a source of the sulfur deposits and H_2S gas dissolved in the spring water due to the reduction of sulfate in via anaerobic bacteria under anoxic conditions.
2. Oil seeps were generated from planktonic kerogen belongs to the type-II, which has a substantial amounts of sulfur associates bitumen rather than H_2S gas.
3. The degree of waxiness reflects the amount of land-derived organic matter depends on source input [39]. The studied oils are characterized by low CV values (-2.88, -2.28, -3.00, -3.47, -0.17, -2.61, -2.66) confirming that these oils are non-waxy and have been mainly originated from the marine organic source deposited under anoxic conditions. The origin of the oil seeps is marine non-waxy oil generated from marine source rock deposited in an environment of low to high salinity with little participation of bay and estuary under anoxic conditions and belongs to non-gas field origin.
4. The high variability in NSO% values (5.4% to 26.8%) indicates that samples have been subjected to a disparity biodegradation. NOS% is positively correlated with both aromatic and saturated compounds; the coefficient of determination (R^2) was computed to be 0.855 and 0.713 and defined by the exponential equations: $Y=1.355e^{0.35x}$ and $Y=1.098e^{0.83x}$ respectively.
5. The values less than 1.0 of the steranes ratio (C28/C29) in all samples indicate an oil of marine origin generated from source rock older than Jurassic and Cretaceous rocks. Dinosteranes were identified in all samples and documented in Figure 5 to express as mark for the dinoflagellates. Moldowan and Talyzina [23] stated that the Dinosteranes are used as a mark for the dinoflagellates that were originally considered as existing only in Triassic and younger age.

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