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Determining Source Rock and its Characteristics Using Organic Geo-Chemistry Derived from Parent Rock Evaluation, Separation, and Columnar and Gaseous Chromatography on Cretaceous Units in Central Iran at Khor-Biyabanak

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Abstract

Recently, the investigations made on rocks of cretaceous units at Central Iran have revealed source rocks and their characteristics (origin, amount, and type, maturation of organic material, hydrocarbure(Hydrocarbon) generation ability and sedimentary organic material environment). The information obtained from investigation and evaluation of cretaceous rock units at Khor-Biyabanak region using following methods have led to the determination of the source rocks with some weak to medium organic material from the downstream to upstream of the section (underlying-intermediate cretaceous towards upstream cretaceous) in the region such as evaluation of source rock, separation of Bitumen, columnar Chromatography, and aseous Chromatography. With due regard to the amounts of TOC, HI, Tmax, S1, S2, PI, EOM, HCS, SAT/ARO, CPI, Pr/Ph, pr/n-c17, ph/n-c18, and the ratios, graphs, and derived peak values, it can be claimed that the type of organic materials present in the source rocks are Classes II and III Kerogens. The maturation of existing organic material in the source rocks is high and shows approximately the ending oil generation window and last stages of Catagenesis (Katagenesis). The origin of the organic material is also a marine and continental mixture which currently is capable to generate humid and dry gas in the existing source rocks. Also, the formation environment of existing source rocks is regenerative, and quasi-regenerative-marine.

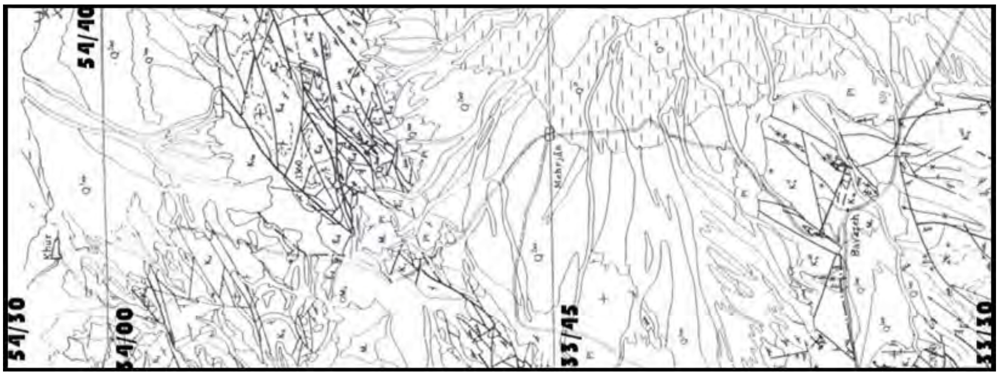
Keywords: Source Rock, Organic Geo-Chemistry, Gaseous Chromatography, Khor-Biyabanak

Introduction

This section is located at Central Iran zone at Khor-Biyabanak section being one of the suburbs of Isfahan Province. The location of segmentation is nearly 50 km to the south-east of Khor-Biyabanak at 33.35 northern latitude and 54.35 to 54.37 eastern longitudes. The cretaceous units at this section include the below facies (Fig. 1). At the region the cretaceous with shale facies of 3000 m thickness are seen as being grey to green and dark grey to sandy laminated, silt, lime, marly shales and scarce occurrences of thin lime layers and the age of the region is determined by underlying cretaceous (Albian). These shales gradually turn into other Albian facies and particularly into orbitolinids lime. Then, in the upstream cretaceous this series transform into carving sandy lime facies and end up into gypsum containing shale marl. Subsequently, carving-regenerative grey to muddy hued limes that occasionally are inclined to brownish color and at upper part are inclined towards yellow and brown with regular stratification are seen. Then, the above series are turned into purplish grey marly limes with reasonably regular bedding with the inevitable existence of sandy and marly limes with thick strata. All these above items were observed at the region under study.

Methodology

In order to determine the source rock at the region under study aimed to perform organic geo-chemical study of cretaceous units, 100 earth surface specimen pieces were collected. Since in most cases, the samples from flat plain undergo corrosion, oxidization and micro-degradation, sample taking was made as much as possible at sections with fresh surface (not polluted). Initially, the specimens were macroscopically and microscopically reviewed. Due to abundance of organic matter, 29 samples were selected for quantitative and qualitative analysis (using version 3 Rock Eval device). Then using the obtained parameters and especially the total carbon content (TOC), 8 samples with more suitable quality and quantity than other specimens were chosen. In order to separate the bitumen in the samples, sacculation method was used. In this method, first of all rock specimen was grinded (to about 90 mesh) and then placed in cellules test tubes. Using organic solvents such as chloroform and dichloromethane, the organic matter was separated. For the purpose of molecular bitumen (EOM) studies having separated the asphaltene using normal hexane solvent by the use of columnar chromatography method and heptane normal solvent, the existing saturated hydrocarburates in the bitumen were separated. Then, these saturated hydrocarburate specimens were reviewed by means of gaseous chromatography method using Chrompack type gaseous chromatography device, model cp9000.



Figire 1 . Geographical Location of Sections (A-A`) at Khor-Biyabanak Region (Source: Iran Topological Organisation1346; 1: 250000 Topological Map)

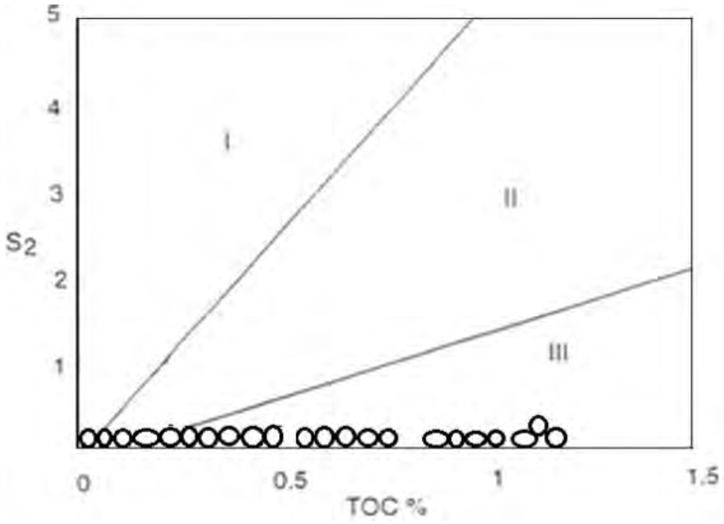


Figure 2. Types of Kerogen at Khor-Biyabanak region according to relation between s2 and TOC resulting from Parent Rock Evaluator

Result and Discussion

Parent Rock Evaluator (Rock Eval) Data

Rock Eval (Parent Rock Evaluator) is used in parent rock as a geo-chemical device for determining the quality and type of organic material, their maturation level, and determining of hydro-generation competency, and generated hydrocarbures. For this reason, 29 samples were tested from the location in question using the above mentioned device into the result shown in attached Table 1. In this device, the parameter Tmax is used as a ripeness parameter of organic material in order to generate oil hydrocarbures. Accordingly, the following classification of oil geo-chemistry is specified for it (Keramati, 1995):

1- Not ripe or immature stage, Tmax< 435 °C
2- Oil formation stage, Tmax= 435 – 470 °C
3- Wet gas – dry gas formation stage, Tmax> 470°C .

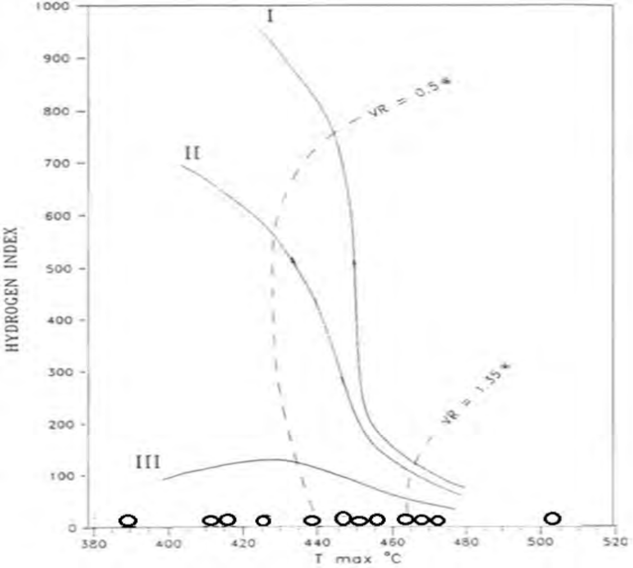


Figure 3 . VAN KREVELEN Graph based on hydrogen index relationship and maximum heat resulting from Parent Rock Evaluation (Rock Eval).

Evidently, different minerals that exist in the rock matrix on the material obtained from Pyrolysis Kerogen have proportioned effects (Peter, 1986) and can eventually affect the Tmax parameter. Clay minerals in rock matrix can reduce the Pyrolysis action from 30 to 85 percent; a fact that is clearly observable in the specimens studied at Golpayegan province. Of course, absorption of material resulting from Pyrolysis in rock matrix generally is more witnessed in poor rocks TOC < 0.5 %. In such rocks even for releasing of Pyrolysis material, rock matrix minerals with higher thermal degree is required. According to above information, and in view of Table (1), the amount of organic matter in the Khor-Biyabanak region samples includes 3 groups of source rocks of the poor type with 0 to 0.5 % organic material, the medium type of 0.5 1 percent of organic material, and the prime type of 1 to 2 percent of organic material (Cooper & Ower 1982). According to the method and the view of Peters (1986), the s1 amounts of hydrocarbures and s2 amount of potential production of hydrocarbure and s1 + s2 are also in the poor range of organic material as above. The amounts of Tmax, i.e. the maximum heat show a vast range and cover the 3 ranges mentioned above. Thus, in the specimen too the Tmax is both affected by the clay matrix minerals and influences their igneous rock samples of the latest cretaceous and their third period. Generally, with due regard to the amount of generation index (P) it can be said that the samples in above mentioned region belong to the oil generation window and Catagenesis and considering the amount of hydrogen index (HI) being in the range of 0-150 milligrams per organic material gram, the present conditions have gas competencies. Using Table (1) and the graph s2 during TOC and HI against Tmax, the type 3 Kerogen is anticipated. Later studies show that the remains of organic material are basically type 2 Kerogen, although some type 3 Kerogen is also contained in the organic material series. Due to the partial oxidization of an organic material during the early Diagenesis stages and with the increase in the majority of Burial Diagenesis, the type 2 Kerogen has convereted into type 3 (Figs. 2 & 3).

Table 1. Assessment data for rock samples from the Cretaceous units in Khor-Biyabanak

sample		Weight	S1	S2	Tmax	GPI	OPI	TPI	TOC	HI	S1+S2	PI S1/S1+S2
B	1	87.3	0.01	0.01	389	0.00	0.50	0.50	0.25	4	0.02	0.5
B	2	83.1	0.01	0.02	452	0.00	0.50	0.50	0.32	6	0.03	0.33
B	3	87.3	0.01	0.01	426	0.00	0.50	0.50	0.12	8	0.02	0.5
B	4	50.3	0.01	0.05	583	0.00	0.17	0.17	1.08	4	0.06	0.17
B	5	47.6	0.08	0.04	464	0.00	0.67	0.67	0.64	6	0.12	0.66
B	6	42.8	0.02	0.02	413	0.00	0.50	0.50	0.64	3	0.04	0.5
B	7	55.8	0.05	0.05	472	0.00	0.50	0.50	0.88	1	0.10	0.5
B	8	43.6	0.02	0.02	438	0.00	0.50	0.50	0.57	3	0.04	0.5
B	9	50.3	0.03	0.01	416	0.00	0.75	0.75	0.39	2	0.04	0.75
B	10	51	0.01	0.03	455	0.00	0.25	0.25	0.74	4	0.04	0.25
B	11	84.4	0.01	0.02	572	0.00	0.50	0.50	1.13	1	0.03	0.33
B	12	88.5	0.01	0.02	563	0.00	0.50	0.50	0.73	2	0.03	0.33
B	13	82.5	0.02	0.02	535	0.00	0.50	0.50	0.93	2	0.04	0.5
B	14	87.3	0.02	0.02	542	0.00	0.50	0.50	1.10	1	0.04	0.5
B	15	89	0.01	0.02	505	0.00	0.50	0.50	0.88	2	0.03	0.33
B	16	88.3	0.03	0.01	468	0.00	0.75	0.75	0.57	1	0.04	0.75
B	17	82.2	0.02	0.00	373	0.00	0.50	0.50	1.27	1	0.04	0.5
B	18	84.4	0.02	0.01	*	0.00	1.00	1.00	0.38	2	0.03	0.66
B	19	88.8	0.02	0.00	450	0.00	1.00	1.00	0.32	0	0.02	1
A	1	84.2	0.14	0.01	350	0.00	1.00	1.00	0.17	5	0.15	0.93
A	2	75.3	0.01	0.01	*	0.00	0.50	0.50	0.00	0	0.02	0.5
A	3	80.9	0.00	0.00	*	*	1.00	1.00	0.01	0	0.07	1
A	4	87.3	0.00	0.00	*	*	*	*	0.24	0	0.01	1
A	5	83.2	0.00	0.00	*	0.00	*	*	0.00	0	0.00	0.00
A	6	76.1	0.01	0.01	*	*	0.50	0.50	0.00	0	0.02	0.5
A	7	83.6	0.01	0.00	*	*	*	*	0.22	0	0.01	1
A	8	79.5	0.01	0.00	*	*	*	*	0.05	0	0.01	1
A	9	80.8	0.01	0.00	*	*	*	*	0.18	0	0.01	1
A	10	85.9	0.01	0.00	*	*	*	*	0.17	0	0.01	1

Separation of Bitumen Data

According to data evaluation by Rock Eval device, eight Type 33 samples that had desirable parameters were selected for bitumen separation in order to be evaluated and interpreted for further investigation. In order to separate the bitumen, the powdered and distributed samples are put in a sacculation device. For 50 grams of the sample 250 – 300 cc chloromethane (chloroform) solvent is usually poured in a balloon and connected at the bottom of the device and a heating device is also connected and adjusted on solvent evaporation temperature of 60 °C. This would take 48 – 72 hours work until the separation is realized. Since the solvents available with us for each test sample were 50 grams and on the other hand, 50 g of each sample under study provides enough bitumen for analysis, thus after required investigations further action was taken using the below discussed method. For a specific sample, solvent containing separated bitumen from the 50 g weight was kept and only 50 g from the same sample is placed in the device for each attempt. Subsequently, the amount of solvent used which would amount to 2500 – 3000 cc when separation of 500 g bitumen is required, is reduced to one-tenth and the possibility to separate the bitumen from each sample into the amount required for testing (even a sample of 50 – 1000 g) is also possible for 50 g with the same consumable solvent. This action has economic advantages. The separation of samples for 200 g of each sample is performed. The solvent containing bitumen of each sample is filtered using no. 41 filter. For the evaporation of consumable solvent, the combined solvent and bitumen inside the balloon are connected to the evaporator. Then the evaporation and recovery of the solvent takes place. The remaining bitumen is put in an already balanced receptacle. After drying using an electronic balance (with 0.0001 g precision) measurement is made and recorded (Table 2). Next, hexagone normal solvent is added to the samples of bitumen and filtered using filter paper no. 42 in order to separate the asphaltene from them and make our measurement and recording of the values. Transfer is made to the columnar chromatography laboratory in order to separate the paraffin, aromatics and resins. For the purpose to ensure there is source rock or not, the above mentioned samples are treated as follows: By using the amount of achieved bitumen (EOM) and in order to put them against the amount of total carbon (TOC) which is determined from the data on parent rock we attempt to determine the source rock. The above mentioned samples in the region at the downstream section are found to be in the ranges of a prime to well-primed source rock and at the upstream section to be a medium, weak and void of organic material (Fig. 4).

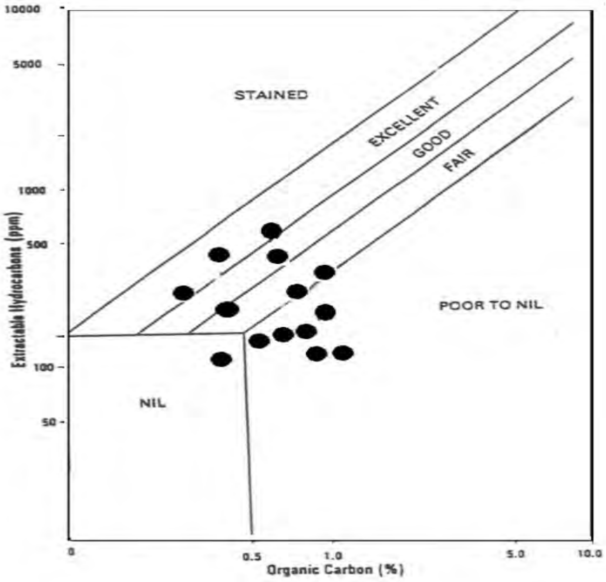


Figure 4 . Data on Rock Eval based on amount of organic material versus bitumen content. POWELL 1978

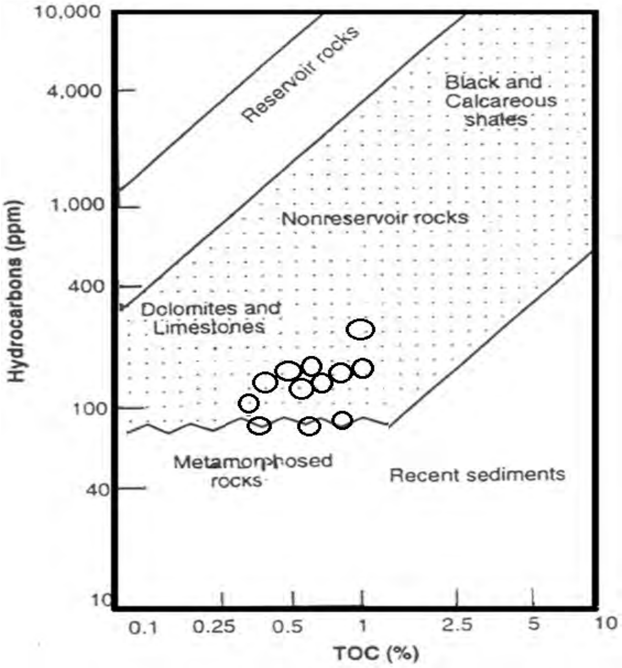


Figure 5. Amount of organic material versus hydrocarbons at the shaded area for the determining of source rock, source rocks with over 70 ppm of organic material (Hant 1979)

Columnar Chromatography Data

Samples taken from asphaltene for separation of bitumen are placed one by one in the device's upper receptacle for segregation of saturated hydrocarbure (paraffin), aromatics, and resins and then 300 – 500 cc pentane normal solvent is poured over them and the solvent containing paraffin is received from beneath the device receptacle. With the seepage of the last solvent drops and having ensured the paraffin is fully segregated by the evaporator from the solvent containing it, the amount of paraffin is measured and kept for later tests. In order to separate the aromatics from the solvent, 300 – 500 cc benzene is used. The method adapted at this stage is similar to separation of paraffin. Next, according to the values measured, the amount of respective resin for each sample is calculated and recorded (Table 2). Using the available data the interpretation of the data is made. The values illustrate that the organic material is highly mature. Also, added to the determining of the maturity on the basis of saturated hydrocarbure frequency and aromatics and particularly their ratio (Sat/Aro) , the determining the type of sedimentary rock and determining it as being a source rock or not can be established by putting the value of organic material (TOC) against the summoned up of saturated hydrocarbure and aromatic (HCS). As explicated in Fig. 5, most of the samples are within the realm of the source rock. We verified the quality of the source rock on the basis of the amount of hydrocarbure (HCs). According to the theory held by Cooper & Ower 1982, since the samples under study are mostly 0 – 30 milligram per 1 gram of organic carbon and/or contain 0 – 300 PPm organic material, thus the quality of the adapted source rocks in the present study are of gaseous type and have probably undergone the oil generation stage. On the other hand, the high level of EOM/TOC justifies the need fro organic geo-chemical studies which have to continue.

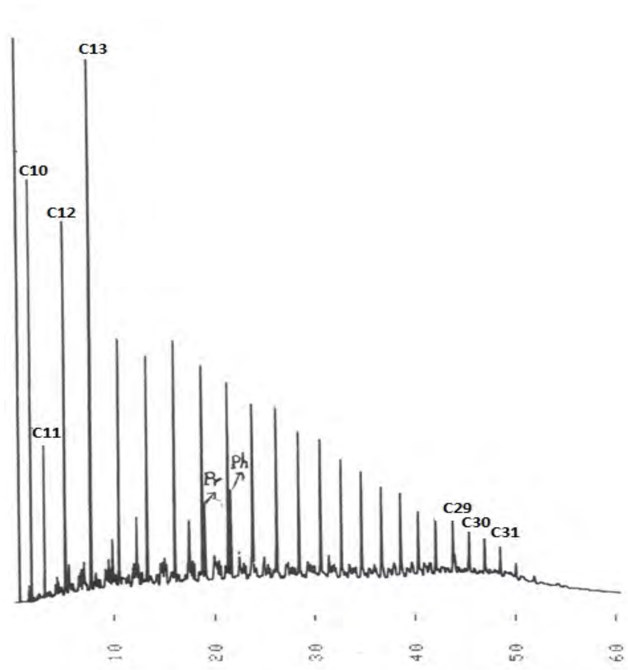


Figure 6 . Gaseous chromatogram of B4 sample

Data on gaseous chromatography (Gc)

In order to obtain information on gaseous chromatography (GC) from the Chrompack device; model: cp9000 which contains a 25 m long capillary column of CP-sil-5, a 60 °C heating program with 270 °C ultimate heating (in 4 °C heat increase per minute during the testing) is used. The dissipation and form of chained normal and chained tributary hydrocarbures on chromatograms attained from the device which are taken as peak values are used. After the previous quantitative and qualitative studies, the organic extraction taken from 7 samples (already obtained from the region which are already prepared and balanced by columnar chromatography as purely saturated hydrocarbures) are transferred to gaseous chromatography laboratory where part of the separated paraffin (structured hydrocarbures) are injected into the CG device by special syringes and by turning on the device in accordance with the pre-determined program and based on molecular weight of hydrocarbures, the light hydrocarbure and ultimately heavy ones are extracted from the chromatograph column and recorded as peak values. Then, using the attached data on peak values, the peak values under study are calculated and measured. Such data as pristance, phytane and their pr/ph ratio, carbonic preference index (CPI) and other values are attained according to table 3, which are to be used for interpretation of the origin of material, sedimentary environment and degree of ripening of source rock. It should be noted that the amount of CPI is derived from the statement below. 1.02 equivalent value of CPI shows the existence of organic material and the values between 1.2 and 5 show the immaturity of organic material.

$$CPI=2\{C23+C25+C27+C27+C29+C31+C33\}/C22+2\{C24+C26+C28+C30+C32\}+C34$$

According to peak samples (Fig. 7), and calculations based on them (Table 3), the Pr/ph ratio is about 1. which represents the high amount of ripening (maturity) of the source rock, and on the other hand, since in some of the samples this ratio is less than 1, then the environment related to source rock is of marine type.

Table 2. **Geo-chemical data obtained from bitumen separation method and columnar chromatography method in the region.**

sample	weight	EOM	Ppm	TOC	EOM/TOC	SAT ppm		ARO ppm		NSO ppm		As pb ppm		HCS ppm		SAT/ARO
B1	100	25.5	255	0.45	56.6	28	71	29	72	21	55	22	60	57	143	0.99
B2	100	29.6	296	0.32	92.5	14	41	13	40	36	106	37	110	27	81	1.03
B4	100	36.7	367	1.08	34	22	80	25	92	41	149	12	46	47	172	0.87
B5	100	55.8	558	0.64	87.19	17	93	12	70	50	280	21	115	29	163	1.32
B6	100	44.9	449	0.64	70.16	20	90	18	81	42	190	20	88	38	171	1.11
B7	100	24.1	241	0.88	27.39	34	81	33	80	23	55	10	25	67	161	1.02
B8	100	19.9	199	0.57	34.91	20	41	21	42	18	35	41	81	41	83	0.98
B9	100	44.4	444	0.39	113.85	14	61	9	40	19	83	58	261	23	1.1	1.52
B10	100	18.9	189	0.74	25.54	21	40	22	41	26	50	31	58	43	81	0.98
B13	100	13.9	139	0.93	14.95	22	31	65	90	10	15	3	4	87	121	0.34
B14	100	23.9	239	1.10	21.73	38	91	26	62	32	77	4	9	64	153	1.47
B15	100	15.4	154	0.88	17.5	26	40	59	91	9	14	6	9	85	131	0.44
B16	100	20.0	200	0.57	35.01	51	1.1	25	50	10	20	15	29	76	151	2.02
B18	100	11.85	118.5	0.38	31.18	25	30	18	21	22	26	35	41	43	51	1.43

Table 3. Data taken by gaseous chromatography method and bulk spectrograph in the Khor-Biyabanak region

N	pr	Ph	Pr/ph	CPI	n-c17	n-c18	Pr/n-c17	Ph/n-c18	C27/c29
B1	1.2625	1.15	1.1	1.15	1.62	1.64	0.78	0.70	0.84
B4	1.1429	1.02	1.12	0.93	1.45	1.47	0.79	0.70	1.09
B6	1.0817	0.98	1.1	1.137	1.51	1.51	0.71	0.65	0.73
B9	0.605	0.77	0.78	0.80	1.10	1.13	0.55	0.69	0.85
B16	1.3133	1.29	1.02	0.89	1.77	1.88	0.74	0.69	1.00
B18	0.9196	0.91	1.01	1.12	1.32	1.30	0.70	0.70	0.95

Also, the amount of CPI is in the ranges of 0.97 – 1.12 which indicates the maturity of organic material of the source rock to be at the last period of Catagenesis. Since the values obtained in Table 3 for environments of some rocks are of regenerative and semi-regenerative type (Fig. 8), then in addition to above facts, as a general term, gaseous chromatography and the chromatograms have the following characteristics:

1- The light paraffin normal hydrocarbures have significant frequency and this characteristic on its own not only justifies the high ripeness of organic material in source rock but also can show the high amount of marine organic material (type 2 Kerogen).

2- Mostly, they have carbine pair precedence at nc14 to nc26 hydrocarbure paraffin reference which can indicate the existence of marine organic material in source rock.

3- In some chromatograms related to source rocks of region 1 a double distribution of chained normal hydorcarbures is observed which represents the origin of continental and marine organic material.

4- Severe micro-carving in some samples is seen, which is the reason for the existence of organic material with marine origin and marine environment (Fig. 7).

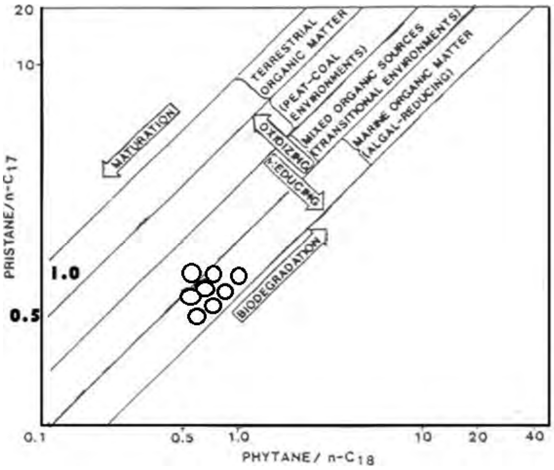


Figure 7 . Pr/n-c17 ratio graph against n-c18 to show the dominating conditions on organic material and source rock pile-ups.

Conclusion

1- The amount of organic material in Khor-Biyabanak region shows as average medium to weak source rocks from downstream section (underlying intermediate cretaceous) towards the upstream of section (upstream cretaceous) which is verified by the relationship graph between TOC and bitumen, too.

2- At the underlying section of the region a minimum amount of organic material is considered to be a potentiality for existence of the source rock. Therefore, samples with 0.25 to 0.5 percent of organic material and more then 0.5 percent of organic material are more suitable for further precise evaluations. The amount of organic material shows that in this region most of the underlying intermediate cretaceous sediments had favorable conditions for organic material deposition and for the formation of source rock and had declined towards the upstream cretaceous of organic material pile-up.

3- The amounts of Tmax, s1, s2, PI of the samples also show the approximate ending of horizontal window and terminating stages of Catagenesis. So from the present source rock, humid and dry gas can be expected. Also, with reference to graphs for S2 and TCC and also the group of HI against Tmax it is shown that the Kerogen is apparently type 3. By considering the realm of changes in the amount of organic material and the Kerogen types and the sedimentary environment, and considering there is normal distributed alkanes at gaseous chromatography and normal alcines exists at downstream from CI0 to CI8 in some of the samples, it is deferred that the organic material considered are of marine type and most probably are type 2 Kerogen. This fact is also verified by derived graphs that depict the environment as being regenerative and semi-regenerative and show the origin of organic material to be of alga and bacteria. This by itself is a proof of the existence of a Kerogen of a better type and probably of the second and third type or of the second type in source rocks in the region. Also, with due regard to the pr/ph changes that are in less than 1 range and around 1, it is verified furthermore that the source rocks in the region under study is in marine environment.

4- The high maturity level of organic material of source rocks has caused the preliminary studies type 3 Kerogen to be estimated but in fact this is not the case. Maturity of organic material in view of the values of Tmax and the effect of clay minerals and other existing minerals in the rock matrix, the little amount of S1, S2, S1 + S2 and the amount of production index (PI) is equivalent to about 0.4. The dispersion of saturated hydrocarbures, aromatics, and nonhydrocarbures (asphaltene and resin), show the high value of SAT/ARO ratio which shows a range higher than 0.5 to 0.9. The graph resulting from placing the hydrocarbons percentage against their values in milligram, with the CPI values in the range of about 0.79 to 1.135, and the amount of Pr/PH at about 1 indicate that the organic material of source rocks exhibit the ending stages of Catagenesis, oil generation window, and finally the generation of humid and dry gas.

5- According to detailed investigations of the gaseous chromatography, the following information regarding organic material of source rocks in cretaceous units of the region under study can be stipulated:

- Existence of light paraffin normal hydrocarbures with significant frequency which represents the existence of a high amount of marine organic material (types 2 and 3 Kerogens) and shows the high maturity of organic material in the source rocks.
- Preference of carbonic pairs in nc14 to nc26 paraffin hydrocarbures at gaseous chromatographic spectra which represents the existence of marine organic material of source rocks.
- The infra-carbon precedence at gaseous chromatography spectra in little amount of samples of region under study including c7 at reference nc11 to nc13 is seen which is quite noteworthy.
- Bilateral distribution of chained normal hydrocarbures in some of the gaseous chromatograms, which represents the origin of mixed continental and marine organic material.
- Micro-carving of some samples is the reason for the existence of organic material with marine origin and marine environment.

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