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Research Article

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Organic Geochemistry of Miocene Sediments (Hafik and Karacaören Formations) in the Sivas Basin, Turkey

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Abstract Miocene sedimentary units (Hafik and Karacaören Formations) have been deposited in a lateral transition in the Tertiary Sivas Basin. Organic geochemical properties of these sediments in the basin have been determined by means of total organic carbon (TOC) analysis, rock-eval pyrolysis, vitrinite reflectance data and organic petrography investigation. The total organic carbon content (TOC)of sediments from the Miocene (Hafik and Karacaören Formations) are between 0.07 and 1.46% indicating that these formations are poor to moderate in organic matter. Rock-eval analysis yield low hydrogen index (HI) (52-98 mg HC/g TOC) and oxygen index (OI) (34-89mgCO_2/g TOC) values for all samples. The dominant organic matter is type III kerogen. The hydrocarbon-generating potential is very low. The vitrinite reflectance (*Ro*) value is between 0.21 and 0.51%. The average hydrocarbon potential (S1+S2) is 2.38 kg/ton of rock (ranging from 1.15 to 3.42) .The average *Tmax* is 402^{o}C (ranging from 377^{o}C to 435^{o}C). The organic matter content is richer in the sediments of the Karacaören Formation than in the sediments of the Hafik Formation. The Miocene units are dominated by planty, woody, coalified materials (80 to 90%) and amorphous kerogen (10 to 20%)

Keywords Organic geochemistry; Miocene; Sivas Basin; Turkey

1. Introduction

The Miocene deposits (Hafik and Karacaören Formations) are widely distributed in the surface of the Sivas Basin (Turkey) (Figure 1). These sediments show complex thickness and facies changes. Hafik Formation is represented by conglomerate, evaporites and limestones overlain by a 1400 m sequence dominated by siltstones with gypsium interbedded with fining-upward sand bodies. The conglomerate contains serpentinite derived from a provenance area which was uplifted during the Late Oligocene deformation event. The sand bodies are highly interclastic and contain abundant plant debris. This thick sequence records meandering fluvial deposition of highly fluctuating discharge type in a flood plain area of high subsidence rate and arid climate. Karacaören Formation is composed of thick-bedded sandstones and conglomerates which in turn are overlaid by 50 m of silty sandstones of meandering fluvial origin (Figure 2). This meandering fluvial sequence includes nonmarine bivalvesand gastropods and thin allochtonous coal seems, recording interfluvial lacustrine and swamp deposition. Farther to the north and west, the higher parts of the sequence pass up into 300 m of siltstones and marine limestones, apparently equivalent to the marine mudrocks seen elsewhere in transition in the basin. The thickness varies between 500 and 2000 m[1]. Several geological work have been performed [2-6] and [7]. Detailed geochemistry studies have also been carried out and the most important include the work of [8-13]and [1]. The aim of this study is to characterize theorganic geochemistry of the Miocene sedimentary rocks of the Sivas Basin, to determine their kerogen type, and to assess their hydrocarbon source potential.

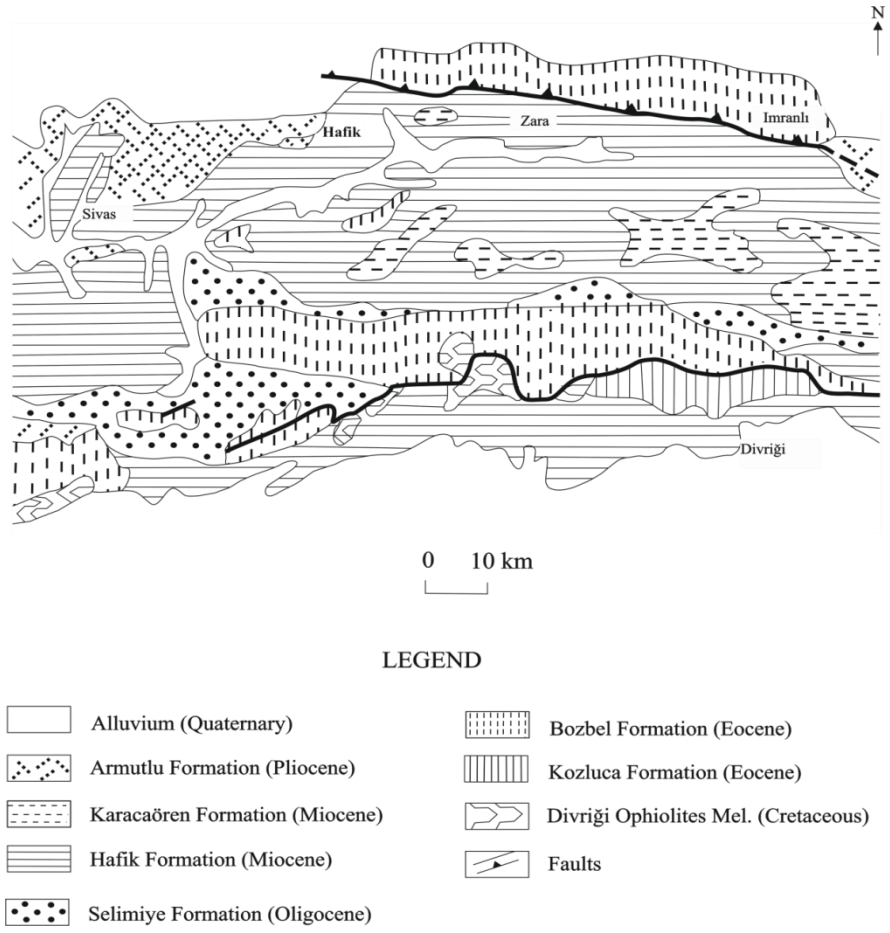

Figure 1: Simplified geological map of the Sivas Tertiary Basin [1].

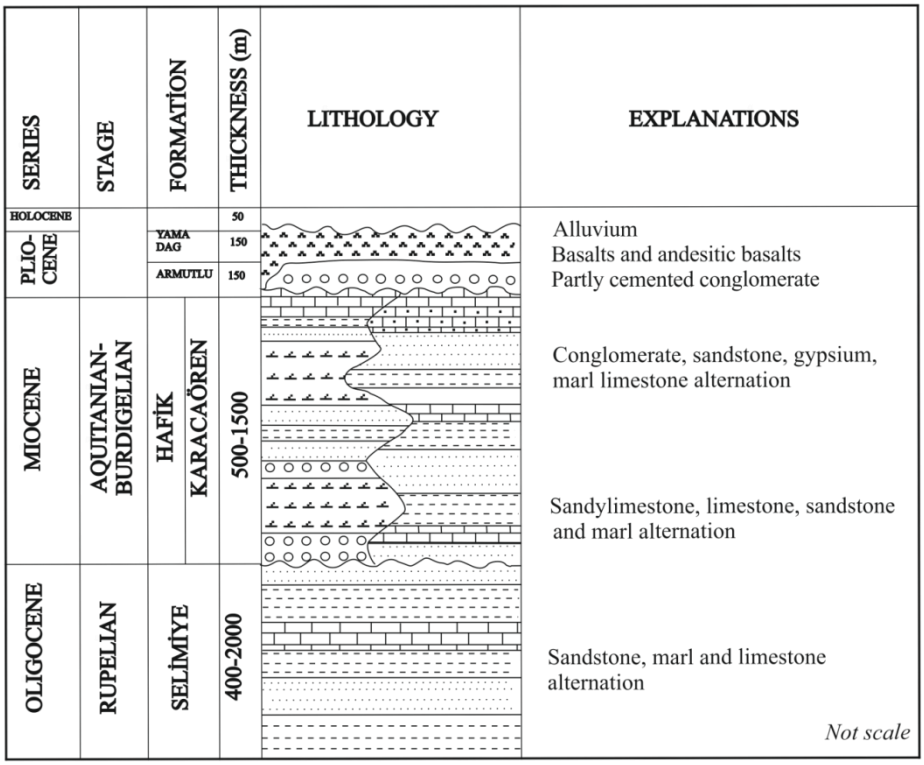

Figure 2: Generalized stratigraphic section of the Miocene Units [1]

Materials and Methods

Outcrop samples were collected as deep as possible below the surface in order to minimize the effects of weathering. The following geochemical techniques were used to characterize organic matter. Disseminated organic matter from Miocene sediments in the Sivas Basin was studied using organic geochemical analysis of 48 samples. These samples were collected from different locations being of Miocene age. Concentrated organic material was sampled from sandylimestone, marl and limestones. The hydrocarbon potential of the sedimentary rocks was determined performed by Rock-Eval pyrolysis [14]. The total organic matter contents of the samples was determined using a Leco elemental analyzer in the Cumhuriyet University laboratories at Sivas(Turkey). Vitrinite reflectances were measured at the MTA laboratories (Ankara/Turkey). Rock-Eval pyrolysis was also carried out at the Geochem Laboratory (Chester, UK).

Results and Discussion

Total organic carbon (TOC) values were measured on 15 samples of the Miocene units (Hafik and Karacaören Formations) from the Sivas Basin. The obtained data show that the total organic carbon values are between0.07 and 1.46% (Table 1). The organic carbon content for the Hafik Formation sediments range from 0.07 to 1.46%, with an average around0.47%; for the Karacaören Formation the TOC values range from 0.05 to 1.72%, with an average of 0.54%; for the Miocene they range from 0.07 to 1.46%, with an average of 0.50%. The organic matter content is richer in shelf sediments such as limestone [1].

Table 1: Total organic carbon (TOC) data of the studied samples [1]

Formation	Sample No	TOC (%)
Hafik	H.1	0.07
	H.2	0.15
	H.5	0.16
	H.6	0.65
	H.7	1.46
	H.18	0.11
	H.19	0.73
	H.20	0.81
	H.21	0.09
Karacaören	Ka.9	1.28
	Ka.11	0.52
	Ka.13	0.40
	Ka.14	0.25
	Ka.131	0.61
	Ka.141	0.15

Rock-eval pyrolysis of whole rock provides information on the quantity, type and thermal maturity of the associated organic matter[15]. Table 2 illustrates the maximum, minimum and mean values of rock-eval analysis of the Miocene samples.These values are as follows: the average hydrogen index (HI) is 79 mg HC/g TOC (ranging from 52 to 98)[1].

Table 2: Organic geochemical data of the studied samples [1]

TOC	S1/S1+S2	S2	S3	Tmax
Min. 0.07	Min. 0.15	Min. 0.77	Min. 0.82	Min. 377
Mean. 0.49	Mean. 0.24	Mean 1.88	Mean 1.04	Mean 402
Max. 1.46	Max. 0.33	Max. 2.90	Max. 1.32	Max. 435
S1	**HI**	**OI**	**S1+S2**	***Ro* (%)**
Min. 0.38	Min. 52	Min. 37	Min. 1.15	Min. 0.21
Mean 0.47	Mean 79	Mean 44	Mean 2.38	Mean 0.30
Max. 0.52	Max. 98	Max. 89	Max. 3.42	Max. 0.42

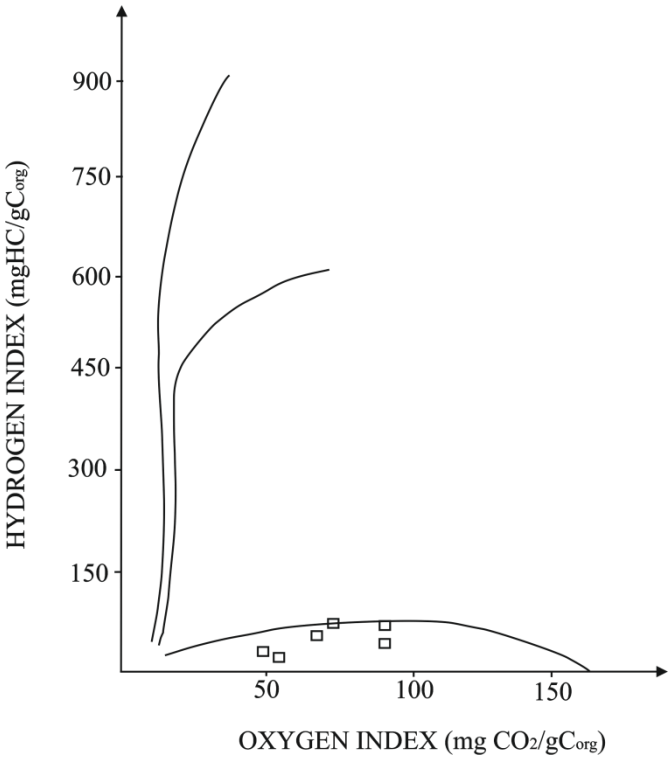

Figure 3: Kerogen type plot of rock-eval data for Miocene units of the Sivas Tertiary Basin [1].

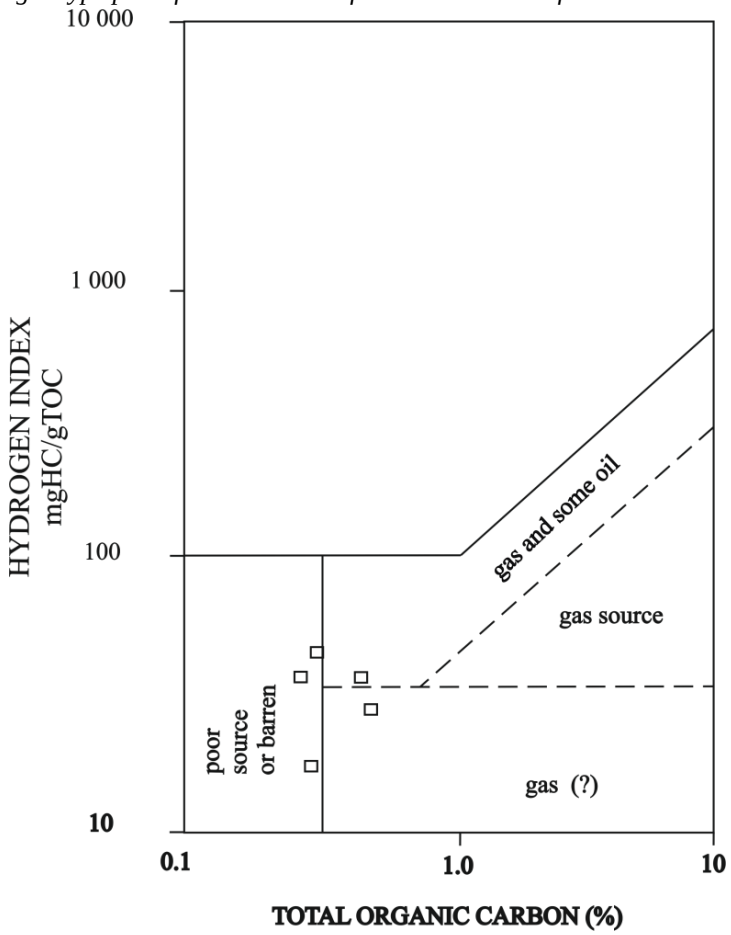

Figure 4: Sources richness plot of the Miocene Units takenfrom [1 and16].

And the average hydrocarbon potential (S1+S2) is 2.38 kg HC/ton of rock (ranging from 1.15 to 3.42) (Table 2). The average *Tmax* is 402°C (ranging from 377°C to 435°C). This organic matter can be classified type III kerogen on the HI, OI diagram [17] (Figure 3). Kerogens are dominated by terrestrial (planty, woody and coaly) organic matter (80-90%) with lesser amorphous organic matter (10-20%).The samples showed vitrinite reflectance data averaging 0.30% (0.21 to 0.51%) (Table 3)[1].

Table 3: Vitrinite reflectance data of the studied samples [1]

Formation	Sample No	Vitrinite reflectance(%)
Hafik	H.6	0.27
	H.19	0.42
	H.20	0.23
Karacaören	Ka.4	0.23
	Ka.9	0.40
	Ka.44	0.23
	Ka.47	0.40
	Ka.49	0.21
	Ka. 54	0.23
	Ka.97	0.22
	Ka. 11	0.36

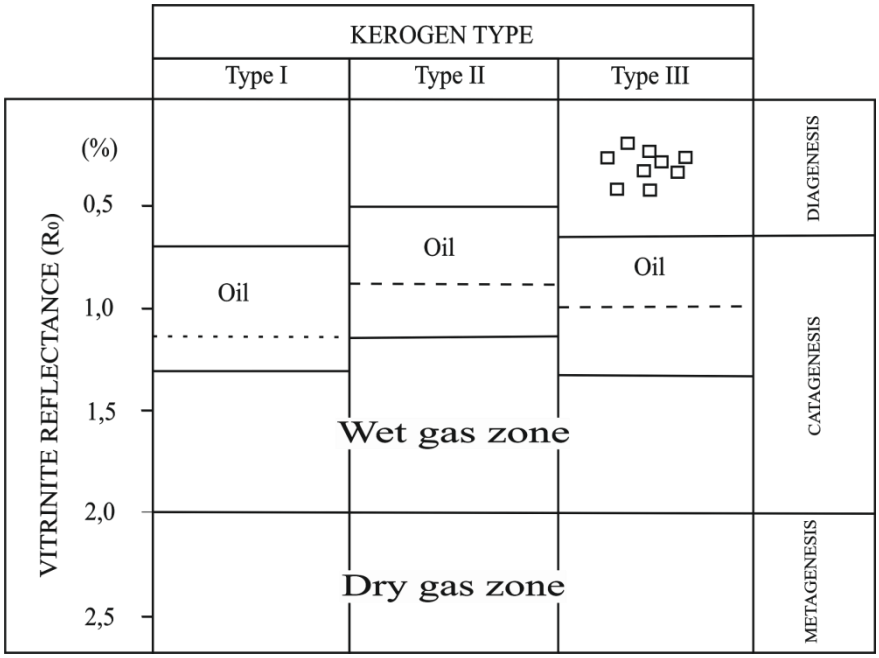

Figure 5: Approximate boundaries of oil and gas zones in term of vitrinite reflectance and kerogen types[17] and distribution of the studied samples [1]

The average hydrogen index of marl and limestone from Miocene sediments is calculated to 0.51mg HC/gTOC and the organic matter content of these sediments is therefore poor to medium. The average values of *Tmax* and vitrinite reflectance show anim mature stage for the organic matter of Miocene sediments. The hydrocarbon potential results are very low, suggesting that this section can not be considered as source rock (Figure5). The sediments have extremely high sedimentation and low to medium TOC values. The data from Miocene sediments show the 'oxic deep-water' conditions [18]. Based on the average values of the hydrogen index and the total organic carbon of all the sedimentary section studied, the Miocene sediments appear to be poor source rock (Figure 6) [1].

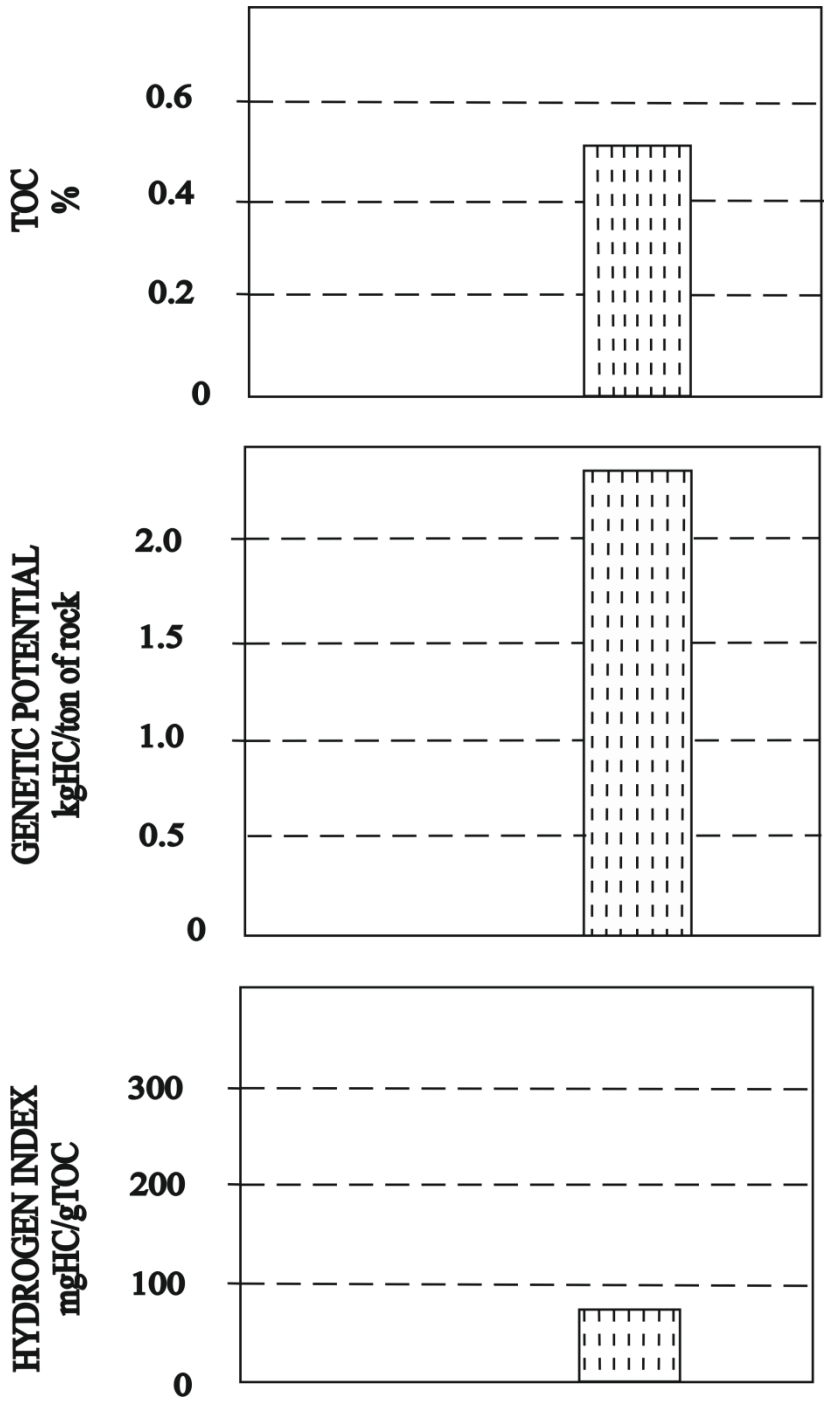

Figure 6: Results of evolution of total organic carbon and petroleum potential by rock-eval pyrolysis of the Miocene Units from various locations of the Sivas Tertiary Basin, Turkey [1]

Conclusion

The samples from the Miocene units present TOC contents (mean value 0.49%), hydrogen index (mean value 79 mg HC/g TOC), vitrinite reflectance (mean value 0.30%) and *T*max (mean value 402 ^{o}C) data. These data suggest that such sediments also can not be considered as source rock. The dominant organic matter is type III kerogen. The organic matter content is richer in the sediments of the Karacaören Formation than in the sediments of the Hafik Formation. The hydrocarbon-generating potential is very low. The composition of Miocene sediments plot in the organic facies derived from shelf sediments and terrestrial sediments.

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