DEPOSITIONAL ENVIRONMENT CHARACTERISTICS OF UPPER CRETACEOUS SEDIMENTS IN HEKIMHAN BASIN (EASTERN ANATOLIA REGION, TURKEY): A BIOMARKER AND CARBON ISOTOPE APPROACH

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ABSTRACT

Biomarker analysis of soluble organic matter in the sediments such as shale has contributed to our understanding of the characteristics of the depositional environment. In this study, depositional environment properties of Upper Cretaceous sediments in Hekimhan Basin are evaluated by biomarker data and stable carbon isotope ($\delta^{13}\text{C}$) values. To ascertain the biomarker features of the aliphatic fractions, GC and GC-MS analyses were realized on the studied shale and limestone samples. Investigated shale samples have generally low ($< 0.5\%$) the total organic carbon values, however, the amount (0.11-5.92%) of organic matter within limestone are slightly higher than shale levels. Hydrogen index values of limestone and shale samples vary between 0.0 and 629 mgHC/g TOC and between 0.0 and 42 mgHC/g TOC, respectively. The odd-numbered and even-numbered *n*-alkanes ranges between the C_{15} and C_{27} , which are among the definable components, are close to each other in terms of abundance. There are *n*-alkanes, especially short-chain ($< n\text{-C}_{21}$) and medium-chain ($n\text{-C}_{21}\text{-}n\text{-C}_{25}$) as well as long-chain *n*-alkanes ($> n\text{-C}_{25}$) like C_{26} and C_{27} , in clayey limestone. The diasterane/sterane ratio in the samples is between 0.19 and 0.60. Besides, the sterane/hopane ratio being high (> 2) and $\text{C}_{26}/\text{C}_{25}$ tricyclic terpane ratio (0.18-0.33) shows the marine precipitation conditions. The moretane/hopane, norhopane/hopane, $\text{C}_{24}/\text{C}_{23}$ tricyclic terpane and $\text{C}_{19}/(\text{C}_{19}+\text{C}_{23})$ tricyclic terpane ratios show the carbonate depositional conditions and, the 18 $\alpha(\text{H})$ -oleanane has been determined and refer to Cretaceous or younger age. The existence of C_{35} homohopanes, hopane index (< 1), high $\text{C}_{35}/\text{C}_{34}$ homohopanes (> 0.8) also supports this result. The $\text{Ts}/(\text{Ts}+\text{Tm})$ ratios define the marine deposition conditions (suboxic), like the decrease in C_{31-35} homohopane distribution and the $\delta^{13}\text{C}$ values (-25.18‰ and -23.48‰).

Keywords: Eastern Anatolia, Hekimhan Basin, organic geochemistry, biomarker, $\delta^{13}\text{C}$.

INTRODUCTION

The Hekimhan Basin is located on the Southeastern Anatolia Edgefolds of the Anatolian Tectonic complex separated by [1], and positioned in the southern side of the Anatolids (Fig.1a). The studied area formed as part of the northern margin of the Taurides during the collision of the Inner Tauride Ocean and the İzmir-Ankara-Erzincan ocean. According to the general stratigraphic characteristics of the study area, the Hocalıkova ophiolite, which is in the base, and pelagic sediments possibly originated from internal Torids Ocean on the North. This unit is obducted as imbricate by braided stream, deltaic Karadere Formation deposited in marine, and with Campanian pebble-sandstone-mudstone alternation; and lateral and vertical transition with the Hekimhan Formation,

which is precipitated in shelf conditions in the upper level. There are the Hasacelebi Volcanites on the upper side.

The Cretaceous sequence, which progresses with Hyk Limestone [2] and Zorbehan Dolomite, is in obduction position improperly in northern areas, and with Akpınar Formation, which is precipitated in shelf-lagoon depositional environment in southern areas that are as old as Paleocene-Mid-Eocene (Fig.1b, c).

Figure 1. Simplified geological map (modified from [2]) and location of the study area within the Anatolian Tectonic Complex, with sample locations.

Upper Cretaceous Hkimhan Formation consists of pebble with sandstones, limestone, sandstones, and sandstone-marl-shale alternation on top of them (Fig. 1b, 1c). Lenticular limestone is observed mainly in the lower levels, and olistostromal and channel filling pebbles at various levels together with clayey limestone are observed in the upper levels [2]. The formation is extremely rich in benthic and pelagic foraminifera, rudist etc. pelecypods; and is as old as Upper Cretaceous-Maastrichtian according to paleontological data [2].

In this study, it is aimed to interpret the depositional environment characteristics of Upper Cretaceous sediments especially by using biomarker properties and stable carbon isotope ($\delta^{13}\text{C}$) values.

Figure 2. Stratigraphic columnar sections of the Hekimhan Formation (modified from [2]) and sampled measured sections (locations 1 and 2).

MATERIAL AND METHODS

Upper Cretaceous sediments were evaluated with surface samples from two different sites (Fig.1b, Fig.2). Principally dark-grey, greenish-grey shales and alternated limestones from Hekimhan Formation were sampled. Some shale and carbonaceous samples (>0.5 TOC) were applied with solvent extraction liquid chromatography gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses were done on bulk extracts obtained from four bituminous samples. The aliphatic components acquire by chromatographic fractionation were done according to ASTM (D5307-97, 2002) by Agilent 6850 instrument. Sterane and terpane ratios were compute by integration of peak highs from the m/z 217 (for steranes) and m/z 191 (for terpanes) mass fragmentograms. Biomarker analyses were done in the research laboratories of the Turkish Petroleum Corporation (TP Research Group, Ankara). Furthermore, stable carbon isotopic ($\delta^{13}C$) values for the samples (eight whole rock sample) were measured on homogenized portion of rock sample using GV Instruments Isoprime EA-IRMS equipment according to PDB Standard (ACME Lab, Canada).

RESULTS

Isoprenoids and n-alkanes

The total extract ratio of the analyzed samples varies between 217-91137 ppm, and is extremely high especially in the limestone in L-2. Polar, asphalten and aromatic compounds are dominant in the investigated samples, and the level of saturated hydrocarbons is relatively less (20-21.35%). Aromatic hydrocarbons are at the rate of 17-30%, and NSO+polar compounds are at the rate of 52-68%.

The odd-numbered and even-numbered *n*-alkanes ranges between the C₁₅ and C₂₇, which are among the definable components, are close to each other in terms of abundance. There are *n*-alkanes, especially short-chain (<*n*-C₂₁) and medium-chain (*n*-C₂₁-*n*-C₂₅) as well as long-chain *n*-alkanes (>*n*-C₂₅) like C₂₆ and C₂₇, in clayey limestone (Fig.3).

Steroids, hopanoids

Sterane and terpane characteristics of investigated unit were determined for shale and carbonaceous samples with *m/z*191 and *m/z* 217 chromatograms (Table 1, Fig. 4 and 5). While the clayey limestone samples from the Hekimhan Formation contains high C₂₉ (C₂₉>C₂₇≥C₂₈), limestone and bitumen sample (MH-24 and MH-30) from location 2 contain high C₂₇ sterane (Table 1).

Based on the triangle diagram of homolog C₂₇-C₂₈-C₂₉ series (Fig. 6) that indicate the organic matter composition in petroleum and kerogen, abundance of C₂₈ sterane indicates green algae and diatoms, abundance of C₂₇ indicates red algae and planktons, and abundance of C₂₉ sterane indicates high plants and red and green algae [3]. Among the samples inspected, while C₂₉ content ratio is higher particularly in shale and biomicritic limestone samples, ratio of C₂₇ is higher in biosparitic limestone.

Table 1. Organic geochemical (biomarker) results of investigated samples

PARAMETERS	SAMPLE NO						
	MH-14	MH-16	MH-19	MH-22	MH-24	MH-29	MH-30
Diast/(Diast+Reg.St) R., C ₂₇	0.47	0.29	0.60	0.19	0.29	0.27	0.23
ββ/(ββ+αα) Sterane R. (C ₂₉)	0.42	0.29	0.37	0.30	0.52	0.48	0.45
20S/(20S+20R) Sterane R. (C ₂₉)	0.39	0.29	0.32	0.30	0.53	0.49	0.43
C ₂₇ /C ₂₉ Sterane R.	0.46	0.24	0.52	0.62	1.57	1.28	1.34
C ₂₉ /C ₃₀ Sterane R.	0.69	1.84	2.76	3.01	2.53	2.51	2.51
Ts/(Ts+Tm) R.	0.12	0.12	0.13	0.11	0.12	0.12	0.11
22S/(22S+22R) (C ₃₁)	0.45	0.45	0.46	0.40	0.46	0.46	0.48
Moretane/Hopane R.	0.31	0.31	0.31	0.31	0.19	0.20	0.25
C ₃₅ (22S)/C ₃₄ (22S) Hopane R.	1	0.85	0.86	1	1	1	1
C ₂₃ T/C ₂₃ TT+C ₃₀ H	0.75	0.63	0.73	0.57	0.77	0.76	0.68
Diahopane/C ₂₉ Ts R.	1.60	1	1.33	0.80	1.25	1.26	1.97
Sterane/17α Hopane R.	2.32	2.39	2.01	1.97	2.34	2.32	2.08
C ₃₅ /C ₃₁ -C ₃₅ HI	0.15	0.15	0.14	0.12	0.13	0.12	0.16
% C ₂₇ , % C ₂₈ and C ₂₉ Sterane R.	36,22,40	15,22,63	29,27,44	40,25,35	50,12,35	49,13, 35	51,14,35
C ₃₁ HH(R)/C ₃₀ H R.	0.83	0.5	0.89	0.44	0.52	0.51	0.54
C ₂₄ / TT R.	0.39	0.39	0.39	0.40	0.41	0.41	0.43
C ₁₉ /C ₁₉ +C ₂₃	0.23	0.21	0.18	0.16	0.24	0.23	0.14
C ₂₄ Tetracyclic Terpane/C ₃₀ Hopane	3.83	2.35	3.75	3.41	3.38	3.56	2.63
C ₂₆ /C ₂₅ Tricyclic terpane R.	0.20	0.25	0.18	0.30	0.33	0.32	0.33
Norhopane/Hopane	6.94	4.77	7.81	3.41	5.62	5.59	5.17

It could be said that especially C_{29} in the composition results from brown-blue green algae in addition to low terrestrial organic matter content [4], [5]. This data is coherent with the low ratio of woody and coaly organic matter determined in the organic petrographic evaluations.

Figure 3. Gas chromatograms of C_{15+} saturated hydrocarbons in extracts from Hekimhan Formation

Figure 4. m/z 217 mass chromatograms for the studied samples.

The diasterane/sterane ratio in the samples is between 0.19 and 0.60 (Table 1). The sterane/hopane ratio being high (> 2) shows the marine precipitation conditions [6]. In some samples (MH-19 and MH-22) the 18 α (H)-oleanane has been determined at extremely lower levels (0.13 and 0.08), and refer to terrestrial vegetation and Cretaceous or younger age. C₂₉ 17 α (H), 21 β (H)-norhopane is dominant constituent. Otherwise, C₂₄ tetracycliterpane, C₂₃ tricyclic terpanes are considerable components (Fig.5).

Figure 5. m/z 191 mass chromatograms for the studied samples.

The C₃₁ homohopanes/C₃₀ hopanes ratio is > 0.25 in marine carbonates, marls and shale-type source rocks, and between 0.44-0.89 in the samples that are analyzed indicate marine depositional conditions. The moretane/hopane (0.19-0.31), norhopane/hopane (3.41-7.81), C₂₄/C₂₃ tricyclic terpene (0.39-0.41) and C₁₉/(C₁₉+C₂₃ tricyclic terpene) (0.16-0.24) ratios (Table 1) show the carbonate depositional conditions and related lithology [6]. C₃₀ hopanes and C₃₅ homohopanes show the high bacterial effects and contribution in the samples [7]. C₂₆/C₂₅ tricyclic terpene ratio shows that the samples precipitated in marine

conditions (0.18-0.33) [8]. The existence of C_{35} homohopanes, hopane index (< 1), high C_{35}/C_{34} homohopanes (>0.8) also supports this result [6].

Figure 6. C_{27} - C_{28} - C_{29} regular steranes ternary diagrams showing organic matter types of investigated samples

In the investigated samples the tetracyclic terpane/hopane ratio is between 2.35-3.83 (Table 1). The normal salinity levels of depositional conditions (30-40‰) have been observed with pregnanes which are measured at a ratio that is close to each other in all samples. Although the $Ts/(Ts+Tm)$ ratios give lower values (<1) in carbonate/evaporitic rocks, they are higher in rocks that are rich in silica, and in lacustrine (fresh water) or deltaic environments (>1) [3], [9]. These data also indicate that the environment of formation of the samples that are analyzed is marine carbonate/evaporitic (0.11-0.13). The Pr/Ph ratio has been detected only in one sample, and indicates anoxic conditions and shale lithology. The C_{31} - C_{35} homohopane is used in interpreting the reduction conditions during deposition of the source rocks. This ratio has also been determined as being similar in all samples (0.12-0.15) indicating low Eh conditions [10]. Low diasterane/sterane and $Ts/Ts+Tm$ ratios define the marine deposition conditions (suboxic), like the decrease in C_{31-35} homohopane distribution [6].

Furthermore, in Hekimhan Formation shale and limestone samples, the $\delta^{13}C$ values are between -25.18 ‰ and -23.48 ‰, and indicate marine organic matters. Although the isotope values of the L-2 limestone samples showed similarities, the sample with the number MH-8, which is taken from shale and limestone levels, is a little different from the others. A 4‰ increase was observed in the change rate, which is $\delta^{13}C$, in n -alkanes with low-medium molecule weight n -alkanes during severe biodegradation [11], [12], [13], [14].

CONCLUSIONS

The total organic carbon values varies between % 0.11 and 5.92 in the grey, greenish-grey-brown shale and limestone samples in the investigated area, and is extremely lower in the shales in the unit ($<0.26\%$), and relatively higher in the alternated limestone ($>0.50\%$). In the samples that are analyzed, the dominant organic matter is the amorphous (65-90%) shales include type III kerogen while limestone samples include type II-III mixed kerogen. The odd-numbered and even-numbered n -alkanes ranges between the C_{15}

and C₂₇, which are among the definable components, are close to each other in terms of abundance. There are *n*-alkanes, especially short-chain (< *n*-C₂₁) and medium-chain (*n*-C₂₁-*n*-C₂₅) as well as long-chain *n*-alkanes (>*n*-C₂₅) like C₂₆ and C₂₇, in clayey limestone. According to the short and medium length chain components and to $\delta^{13}\text{C}$ values (-25.18 to -23.48‰), the marine organic matters are dominant. The normal salinity levels of depositional conditions (30-40‰) have been observed with pregnanes which are measured at a ratio that is close to each other in all samples. Although the Ts/(Ts+Tm) ratios give lower values (<1) in carbonate/evaporitic rocks, they are higher in rocks that are rich in silica, and in lacustrine (fresh water) or deltaic environments (>1). These data also indicate that the environment of formation of the samples that are analyzed is marine carbonate/evaporitic, and the Pr/Ph ratio indicates anoxic conditions. The C₃₁-C₃₅ homohopane ratio has also been determined as being similar in all samples and point out low Eh conditions. Low diasterane/sterane and Ts/Ts+Tm ratios define the marine deposition conditions (suboxic), like the decrease in C₃₁₋₃₅ homohopane distribution and the $\delta^{13}\text{C}$ values.

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