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RARE EARTH ELEMENT (REE) GEOCHEMISTRY AND GENESIS OF OIL SHALES AROUND DAĞHACILAR VILLAGE, GÖYNÜK-BOLU, TURKEY

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Abstract: *The study area is located in the south of Dağhacılar village of Göynük town in Bolu Province, Turkey. This study is a pioneering work in Turkey on the genesis and environmental characteristics of oil shales and other shallow marine-type sedimentary rocks regarding their major and rare earth element contents. The abundances of* SiO_2, Al_2O_3, TiO_2, K_2O *and* Fe_2O_3 *decrease in the following order: claystone > oil shale > marl. CaO and MgO abundances are ranked in the decreasing order as follows: marl > oil shale > claystone. These results reveal the presence of two different genetic groups – detrital and marine. The same groups were also established in the correlation studies of elements. TOT/C and TOC contents of rocks observe the following order: oil shale > marl > claystone, and as a result of variations in redox conditions they also vary in a wide range. Total carbon and total organic carbon are positively correlated with the group representing clays and negatively correlated with CaO, MgO and MnO. That is why TOT/C and TOC are associated with clays. The positive correlations between some major oxides (e.g.* SiO_2, Al_2O_3, Fe_2O_3, TiO_2 *and* K_2O*) and REE might indicate that clays and iron oxy-hydroxyls play an important role in transportation and deposition processes. The only slight negative Ce and positive Eu anomalies and Ce/Ce* and Eu/Eu* values recorded in the depositional environment indicate low oxygenated and anaerobic (reducing) conditions.*

Keywords: *rare earth elements, oil shale, major elements, organic carbon, Dağhacılar.*

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1. Introduction

As reserves of oil are depleting and its price is increasing, other fossil fuels such as oil shales have become more attractive. In some countries, oil is produced from oil shales. In addition, these rocks are an important source of various inorganic elements.

Rare earth elements (REEs) are used as geochemical tracers due to their immobility during weathering and transportation processes. There are well documented works on the origin and environmental characteristics of REEs based on their stable geochemical properties [1–7].

In previous works on oil shales [8–15], REE contents, their associations with certain minerals, the effect of sedimentation rate and redox conditions were investigated. Central and western Anatolian regions in Turkey host various oil shale fields. The oil shales are of Paleocene-Eocene and Middle-Late Miocene age in Turkey [16]. The second largest fossil energy source after lignite is oil shale, therefore it is an important potential energy resource for Turkey [17]. The oil and natural gas reserves in Turkey are of minor scale, and solid fossil fuels account for the primary potential as energy sources [18]. Some areas in the above-mentioned regions have been investigated for organic geochemistry [19, 20] and only a few studies focused on the inorganic element contents of oil shales [21, 22]. However, none of these studies considered major and REE contents.

This study is the first attempt to investigate the origin and environment features of oil shales and other sedimentary units of the Kabalar Formation of shallow marine character on the basis of major and REE contents.

2. Geological setting

The basement in the study area is composed of Upper Cretaceous units which are represented by the Seben Formation consisting of gray, greenish gray limestone, banded marl and sandstones, and the overlying Taraklı Formation consisting of shale, marl and sandstones.

The Upper Cretaceous units are overlain with lateral and vertical transitions by limestones of the Paleocene Selvipınar Formation. They are conformably covered with the Paleocene-Eocene Kızılçay Group composed of Ağsaklar, Kabalar and Dağhacılar formations. The Ağsaklar Formation is the oldest unit of the group and is composed of reddish brown, gray conglomerate, siltstone, sandstone and mudstone alternations. The Kabalar Formation conformably lies above the Ağsaklar Formation. This formation starts with marl and mudstone and continues with oil shale layers and ends to the top with mostly siltstone and shale and limestone layers. Oil shales in the middle part of the Kabalar Formation are brownish-beige colored and partly alternate with marl and claystones.

The thickness of oil shale layers ranges from 0.01 to 9 m with a total thickness of 35 m. The Dağhacılar Formation is the youngest unit of the sequence. This formation conformably overlying the Kabalar Formation is generally composed of reddish-brownish and rarely gray and greenish colored mudstone, sandstone, siltstone and marl (Fig. 1).

(a)

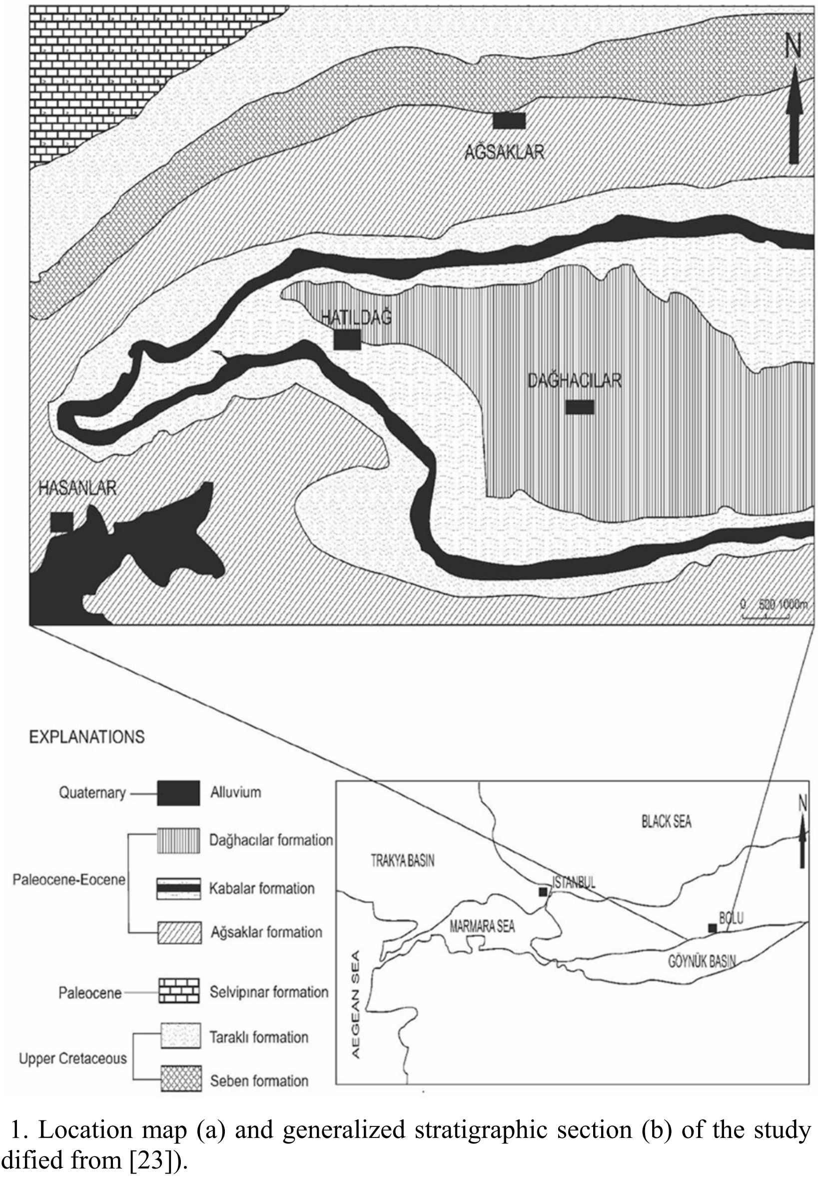


Fig. 1. Location map (a) and generalized stratigraphic section (b) of the study area (modified from [23]).

(b)

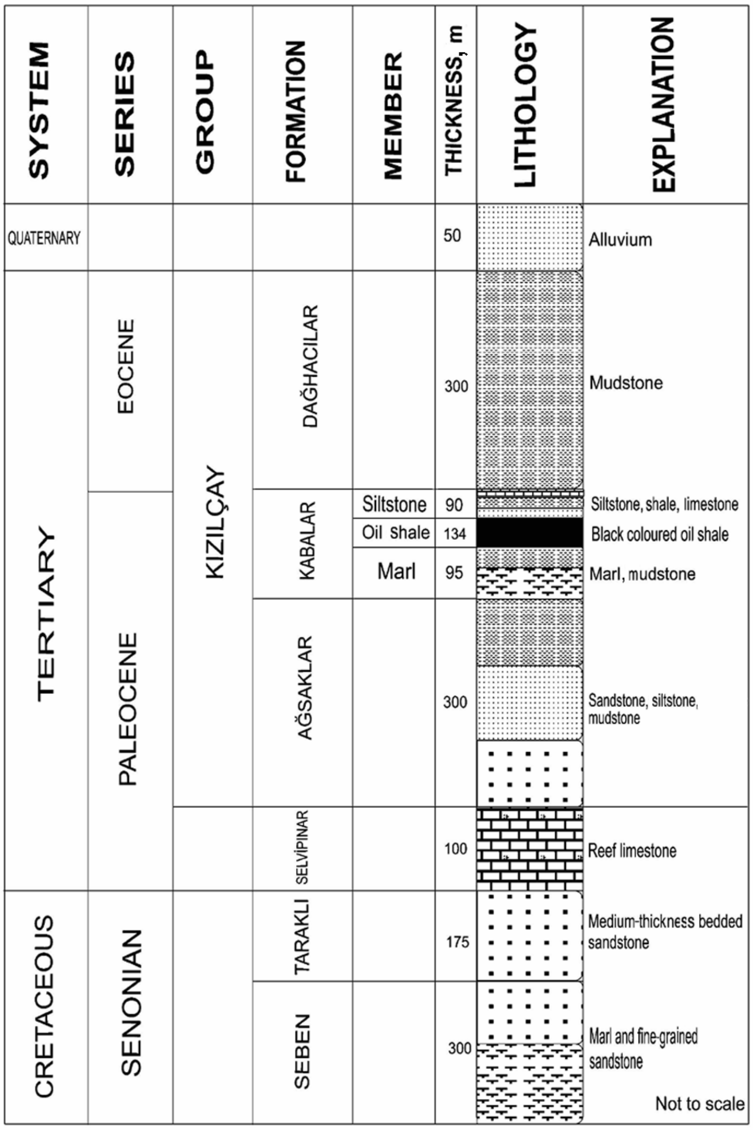


Fig. 1 (continuation).

The stratigraphic sequence outlined above started to be deposited at the end of the Late Cretaceous by a regression from south to north. In the Paleocene, shallow marine limestones (Selvipınar Formation) were deposited in the basin. The region preserved its shallow marine character through the Eocene and oil shales were deposited in sheltered areas behind the barriers where the depth did not exceed 100–200 m [23].

3. Sampling and analytical method

A measured stratigraphic section (MSS) was taken in the Karanlık River site where sedimentary rocks such as oil shale, marl and claystone are well exposed. From this stratigraphic section a total of 45 samples was collected (9 oil shale, 30 marl and 6 claystone samples). The samples were prepared separately for organic and inorganic analyses. Analyses were conducted at Acme Analytical Laboratories Ltd. (Canada) using ICP-ES (major element analysis) and ICP-MS (REE analysis) techniques. The samples were prepared by dilution with lithium metaborate / tetraborate fusion and nitric dissolution processes. The LOI (loss on ignition) of samples was recorded as weight loss after burning at 1000 °C. Element abundances of various rock types were compared and correlation coefficients were computed to investigate the geochemical behaviors.

In order to determine the relation between the elements and organic material, total organic carbon (TOC) analysis was performed for a total of 15 samples (7 oil shale, 6 marl and 2 claystone samples). TOC (%) analysis was conducted at Geochemistry Laboratories of Turkish Petroleum Corporation (TPAO) by the pyrolysis method using the Rock-Eval 6 analyzer. IFP 160 000 (Institut Français du Pétrole) was used as standard.

4. Analytical data and discussion

4.1. Major element distribution and correlations

The abundances of total sulfur (TOT/S), total carbon (TOT/C), TOC and major elements, their variations with lithology and correlations in shallow-marine basin units consisting of claystone, marl and oil shale yield important genetic and environmental information.

TOT/S values are 0.07–1.80% (avg 0.80%) for oil shale, 0.02–1.74% (avg 0.31%) for marl and 0.02–2.25% (avg 0.48%) for claystone (Table 1). Based on the average values, TOT/S is maximum in oil shales. In most marl and claystone samples TOT/S is around 0.02% and its high values in some samples increased the average. For example, 2.25% in claystone (sample KD22) and 1.74% in marl (sample KD26) are much higher values than in other samples.

TOT/C values are 10.48–20.03% (avg 14.53%) for oil shale, 7.66–30.75% (avg 12.73%) for marl and 1.42–17.42% (avg 6.52%) for claystone (Table 1). Based on average values, the abundance of TOT/C obeys the following the order: oil shale > marl > claystone.

TOC in rocks ranges from 0.83 to 13.23% (avg 4.72%) for oil shale, from 0.54 to 6.11% (avg 3.21%) for marl and from 0.27 to 4.75% (avg 2.51%) for claystone (Table 1). As in case of TOT/C, the average values observe the following order: oil shale > marl > claystone. For the three rock groups, the gap between the maximum and minimum TOC values is significantly high

Table 1. Concentrations of major elements and total REEs in all lithotypes

Sample No.	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	TOC	TOT/C	TOT/S	LOI	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	PAAS Ce/Ce*	PAAS Eu/Eu*	UC Ce/Ce*	UC Eu/Eu*
Oil Shale	%														ppm							
KD2	28.24	9.22	4.02	9.87	10.93	0.33	1.53	0.44	0.08	0.09	13.23	14.96	0.53	34.90	39.30	13.23	52.53	2.97	0.87	1.13	0.94	1.13
KD3	18.14	5.90	2.41	14.43	18.13	0.23	0.99	0.28	0.08	0.09	0.83	13.31	0.27	38.90	30.43	10.66	41.09	2.85	0.87	1.11	0.93	1.11
KD5	18.13	2.59	2.09	15.76	22.54	0.17	0.35	0.11	0.06	0.16	1.37	10.48	0.07	37.70	19.26	7.20	26.46	2.68	0.86	1.15	0.93	1.15
KD25	27.27	5.68	3.20	4.16	25.73	1.25	1.68	0.27	0.04	0.13	3.68	10.96	1.18	30.40	43.56	13.66	57.22	3.19	0.85	1.13	0.91	1.13
KD29	19.23	5.78	3.10	4.69	26.55	1.01	2.13	0.30	0.14	0.10	n.d.	15.56	1.80	36.70	41.25	13.85	55.10	2.98	0.83	1.16	0.90	1.16
KD31	25.53	7.57	5.04	6.86	16.13	0.95	2.29	0.45	0.13	0.12	5.49	17.08	0.87	34.60	57.02	22.26	79.28	2.56	0.87	1.15	0.93	1.15
KD39	17.42	5.25	3.23	4.45	29.31	1.25	0.77	0.30	0.18	0.09	3.54	15.12	0.86	37.50	35.96	12.30	48.26	2.92	0.88	1.16	0.95	1.16
KD41	28.54	5.46	4.07	2.73	24.84	0.63	1.15	0.30	0.16	0.09	n.d.	13.30	0.68	31.80	36.62	14.95	51.57	2.45	0.91	1.21	0.98	1.21
KD42	25.65	5.15	3.93	2.43	22.67	0.94	0.97	0.27	0.10	0.09	4.91	20.03	0.95	37.60	33.77	10.86	44.63	3.11	0.90	1.16	0.97	1.16
Average	23.13	5.84	3.45	7.27	21.87	0.75	1.32	0.30	0.11	0.11	4.72	14.53	0.80	35.57	37.46	13.22	50.68	2.83	0.87	1.15	0.93	1.15
S.d.	4.77	1.80	0.91	4.99	5.80	0.42	0.64	0.10	0.06	0.03	4.12	2.97	0.51	2.90	10.22	4.10	14.17	0.25	0.02	0.03	0.03	0.03
Marl																						
KD1	1.27	0.43	0.39	20.25	29.86	0.11	0.06	0.02	0.03	0.08	n.d.	14.04	0.03	47.10	4.19	1.28	5.47	3.27	0.82	0.97	0.88	0.97
KD4	16.84	1.37	1.34	16.41	23.81	0.13	0.18	0.06	0.04	0.16	0.54	11.63	0.07	39.30	11.21	4.63	15.84	2.42	0.83	1.15	0.89	1.14

Table 1 (continuation)

Sample No.	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	TOC	TOT/C	TOT/S	LOI	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	PAAS Ce/Ce*	PAAS Eu/Eu*	UC Ce/Ce*	UC Eu/Eu*
KD6	4.28	0.83	0.50	1.19	29.42	0.06	0.37	0.03	0.03	0.14	n.d.	13.27	0.02	44.80	10.67	3.37	14.04	3.17	0.86	1.37	0.92	1.37
KD8	16.39	5.26	3.15	17.40	19.64	0.34	1.42	0.24	0.03	0.10	n.d.	9.28	0.49	35.60	25.31	9.41	34.72	2.69	0.89	1.27	0.96	1.27
KD9	52.48	0.15	0.13	9.81	14.03	0.06	0.05	0.01	0.02	0.12	n.d.	6.74	0.02	23.10	1.33	0.56	1.89	2.38	0.85	1.13	0.91	1.13
KD10	26.55	5.75	3.34	12.91	18.40	0.21	2.93	0.31	0.04	0.12	n.d.	8.33	1.06	29.10	38.32	11.31	49.63	3.39	0.93	1.16	1.00	1.16
KD11	7.91	0.74	0.34	18.65	27.66	0.09	0.42	0.04	0.22	0.10	n.d.	12.04	0.02	43.40	12.00	7.72	19.72	1.55	0.88	0.87	0.94	0.87
KD12	23.21	6.25	3.34	8.02	24.13	0.16	3.28	0.30	0.22	0.17	n.d.	7.66	0.04	30.60	54.19	20.06	74.25	2.70	0.85	1.15	0.92	1.15
KD14	17.92	1.42	0.76	18.25	21.46	0.06	0.26	0.06	0.01	0.04	n.d.	11.87	0.05	39.30	12.43	4.33	16.76	2.87	0.77	1.17	0.82	1.17
KD15	12.07	3.25	1.73	18.84	22.16	0.10	0.78	0.17	0.01	0.05	n.d.	10.13	0.02	40.30	34.83	11.83	46.66	2.94	0.81	1.13	0.87	1.13
KD16	3.78	1.16	0.59	19.34	27.89	0.09	0.47	0.05	0.01	0.04	n.d.	12.50	0.02	46.10	17.00	4.76	21.76	3.57	0.84	1.11	0.91	1.11
KD17	2.71	0.24	0.26	5.68	47.80	0.02	0.04	0.01	0.01	0.02	n.d.	12.39	0.02	43.10	2.00	0.96	2.96	2.08	0.75	0.89	0.82	0.89
KD18	3.23	0.76	2.95	0.95	49.08	0.04	0.11	0.03	0.12	0.64	0.20	11.81	0.06	42.00	6.12	4.18	10.30	1.46	0.85	1.29	0.92	1.29
KD19	15.89	3.27	2.01	15.63	22.99	0.23	2.13	0.19	0.02	0.10	n.d.	10.28	0.02	37.10	49.74	18.72	68.46	2.66	0.84	1.26	0.90	1.25
KD21	7.26	1.59	0.80	19.34	25.82	0.17	0.71	0.08	0.01	0.03	n.d.	12.26	0.02	43.60	19.72	6.38	26.10	3.09	0.77	1.21	0.83	1.21
KD23	22.41	6.21	2.39	15.06	17.16	0.28	3.06	0.30	0.01	0.07	n.d.	8.26	0.02	32.60	47.17	12.59	59.76	3.75	0.85	1.11	0.92	1.11
KD24	2.40	0.46	0.42	21.51	28.23	0.08	0.07	0.03	0.02	0.03	n.d.	13.10	0.02	46.10	12.21	9.04	21.25	1.35	0.72	1.07	0.75	1.07
KD26	22.22	5.85	3.20	5.81	26.79	1.03	2.02	0.28	0.04	0.15	4.11	11.36	1.74	32.40	42.75	14.57	57.32	2.93	0.89	1.16	0.96	1.16
KD27	20.55	2.89	1.62	16.42	20.71	0.28	0.66	0.15	0.01	0.07	n.d.	9.87	0.02	36.20	22.55	5.94	28.49	3.80	0.86	1.14	0.93	1.14
KD28	5.63	0.76	0.46	19.74	26.99	0.11	0.09	0.04	0.01	0.04	n.d.	12.34	0.02	45.70	9.39	3.06	12.45	3.07	0.78	1.07	0.83	1.07

Table 1 (continuation)

Sample No.	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	TOC	TOT/C	TOT/S	LOI	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	PAAS Ce/Ce*	PAAS Eu/Eu*	UC Ce/Ce*	UC Eu/Eu*
KD30	16.66	5.34	2.96	4.46	30.27	1.00	1.61	0.26	0.09	0.10	3.77	15.36	1.61	37.00	38.71	12.16	50.87	3.18	0.87	1.13	0.94	1.13
KD33	9.42	2.19	1.60	18.60	24.44	0.19	0.38	0.14	0.01	0.07	n.d.	11.37	0.02	42.50	20.27	5.98	26.25	3.39	0.88	1.12	0.94	1.12
KD34	17.18	5.56	2.84	1.77	28.44	1.43	0.86	0.25	0.11	0.09	n.d.	21.88	1.04	41.40	36.15	12.24	48.39	2.95	0.87	1.10	0.93	1.10
KD35	10.08	4.13	2.00	16.65	23.85	0.34	1.06	0.20	0.01	0.07	n.d.	11.11	0.02	41.10	40.16	12.28	52.44	3.27	0.85	1.18	0.92	1.17
KD36	8.09	3.00	2.58	17.60	24.80	0.23	0.82	0.13	0.01	0.07	n.d.	11.68	0.02	42.20	24.92	8.42	33.34	2.96	0.86	1.06	0.92	1.06
KD37	24.81	3.34	3.43	2.04	27.00	0.52	0.73	0.18	0.20	0.09	n.d.	18.01	0.75	37.50	25.29	8.06	33.35	3.14	0.85	1.18	0.91	1.18
KD43	16.89	6.04	2.35	2.80	33.26	1.43	0.88	0.33	0.14	0.25	n.d.	10.87	0.26	35.50	49.45	15.26	64.71	3.24	0.88	1.14	0.95	1.13
KD44	10.57	3.56	2.61	5.51	24.24	1.19	0.52	0.17	0.13	0.10	4.55	30.68	0.86	51.20	24.40	8.40	32.80	2.90	0.88	1.08	0.95	1.08
KD45	4.99	1.41	2.14	2.38	46.07	0.24	0.31	0.06	0.12	0.40	n.d.	13.12	0.53	41.70	13.49	5.07	18.56	2.66	0.82	1.09	0.88	1.09
KD47	12.85	4.77	2.13	3.09	23.98	1.57	0.68	0.23	0.28	0.07	6.10	30.75	1.02	50.20	32.41	10.78	43.19	3.00	0.93	1.13	1.00	1.13
Average	13.92	2.87	1.80	12.17	27.12	0.35	0.91	0.14	0.06	0.12	3.21	12.53	0.31	39.93	23.91	8.21	32.12	2.85	0.84	1.13	0.90	1.13
S.d.	10.41	2.12	1.11	7.29	8.12	0.47	0.92	0.11	0.08	0.12	2.34	5.61	0.51	6.29	15.53	5.01	20.36	0.61	0.05	0.10	0.05	0.10
Claystone																						
KD7	28.51	10.21	5.89	11.89	11.72	0.36	3.09	0.54	0.11	0.14	n.d.	5.97	0.02	27.10	50.73	18.29	69.02	2.77	0.90	1.32	0.96	1.32
KD13	32.79	9.15	4.86	7.73	16.23	0.24	4.71	0.45	0.08	0.15	n.d.	5.65	0.09	23.30	67.04	18.93	85.97	3.54	0.89	1.15	0.96	1.15
KD20	26.37	7.54	3.47	14.19	14.36	0.25	3.42	0.36	0.02	0.06	n.d.	6.56	0.02	29.60	53.72	14.91	68.63	3.60	0.84	1.07	0.91	1.07
KD22	66.14	9.42	4.07	3.18	3.22	0.68	5.28	0.50	0.03	0.05	0.27	1.42	2.25	7.30	51.33	12.61	63.94	4.07	0.88	1.02	0.95	1.02

Table 1 (continuation)

Sample No.	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	TOC	TOT/C	TOT/S	LOI	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	PAAS Ce/Ce*	PAAS Eu/Eu*	UC Ce/Ce*	UC Eu/Eu*
KD38	20.15	5.61	4.25	4.14	24.46	1.21	0.94	0.30	0.11	0.10	4.75	17.42	0.50	38.50	39.62	12.00	51.62	3.30	0.88	1.17	0.95	1.17
KD40	49.08	16.44	4.13	1.82	8.68	1.30	2.81	0.91	0.07	0.09	n.d.	2.10	0.02	14.50	142.58	33.83	176.41	4.21	0.91	1.11	0.98	1.11
Average	37.17	9.73	4.45	7.16	13.11	0.67	3.38	0.51	0.07	0.10	2.51	6.52	0.48	23.38	67.50	18.43	85.93	3.58	0.88	1.14	0.95	1.14
S.d.	17.21	3.67	0.84	5.01	7.20	0.48	1.53	0.22	0.04	0.04	3.17	5.75	0.89	11.12	37.81	8.06	45.68	0.53	0.02	0.10	0.02	0.10

which might be due to changing redox conditions. TOC is positively correlated with Al_2O_3, TiO_2, SiO_2, Fe_2O_3, K_2O and negatively correlated with CaO, MgO and MnO (Table 2). These relations are similar to those of TOT/C; however, values of the correlation coefficient, r, are different. The r values for TOC vs. SiO_2, Al_2O_3, K_2O and TiO_2 are much higher. The values of r for Na_2O and P_2O_5 vs. TOC are close to zero whilst those vs. TOT/C are 0.30 and 0.55, respectively (Table 2).

The correlation between TOC and SiO_2 (r 0.71) is much stronger than that between TOT/C–and SiO_2 (r 0.31), indicating that both silica and detrital quartz have an organic source (Table 2). The strong correlation between TOC and Al_2O_3 and TiO_2 is indicative of the association of organic material with clays.

Although no correlation exists between TOC and P_2O_5, TOT/C is positively correlated with P_2O_5 which may imply that phosphate is not of organic origin and due to its close affinity to carbonate, P_2O_5 is preserved in apatite [5, 7]. Both TOC and TOT/C are negatively correlated with MgO, CaO and MnO. The correlation between MgO and MnO and TOT/C is stronger than that between these elements and TOC (Table 2).

The positive correlations of TOC and TOT/C with SiO_2, Al_2O_3, TiO_2, Fe_2O_3 and K_2O, which are associated with clay minerals, and negative correlations of TOC and TOT/C with CaO and MgO might be indicative of the organic material-clay association and accumulation of Ca and Mg in carbonates (Table 2). The weak correlation of Mn with CaO and MgO may imply that these elements are in close association with carbonates and they are derived from different sources [7, 24].

Table 2. Correlation coefficients of major elements-total REEs-TOC in some oil shales

r	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	TOT/C	TOC	TOT/S	∑LREE	∑HREE	∑REE
SiO_2	1.00	0.65	0.69	-0.49	-0.45	0.26	0.72	0.58	-0.33	-0.10	0.31	0.71	0.57	0.61	0.49	0.58
Al_2O_3		1.00	0.71	-0.22	-0.71	0.05	0.75	0.95	0.13	-0.56	0.37	0.81	0.28	0.70	0.64	0.69
Fe_2O_3			1.00	-0.60	-0.40	0.44	0.81	0.84	0.38	-0.32	0.71	0.61	0.59	0.86	0.85	0.87
MgO				1.00	-0.39	-0.91	-0.38	-0.34	-0.38	0.36	-0.57	-0.22	-0.95	-0.55	-0.40	-0.51
CaO					1.00	0.60	-0.46	-0.60	0.24	0.18	-0.18	-0.64	0.35	-0.26	-0.32	-0.28
Na_2O						1.00	0.36	0.22	0.43	-0.15	0.30	-0.04	0.93	0.57	0.44	0.54
K_2O							1.00	0.82	0.01	-0.10	0.26	0.45	0.56	0.95	0.92	0.95
TiO_2								1.00	0.36	-0.54	0.50	0.72	0.39	0.83	0.81	0.83
P_2O_5									1.00	-0.48	0.55	0.03	0.23	0.28	0.35	0.30
MnO										1.00	-0.63	-0.37	-0.25	-0.20	-0.11	-0.17
TOC											1.00	0.34	0.40	0.38	0.38	0.38
TOT/C												1.00	0.19	0.39	0.32	0.38
TOT/S													1.00	0.69	0.52	0.64
∑LREE														1.00	0.97	1.00
∑HREE															1.00	0.98
∑REE																1.00

The positive TOC-Fe_2O_3 and Fe_2O_3-TOT/S correlations might suggest the association of iron with organic material and pyrite. Considering the positive correlations between Fe_2O_3 and elements in the clay fraction (e.g. Si, Ti, Al) (Table 2), Fe might have two different (pyrite and clay fraction) sources.

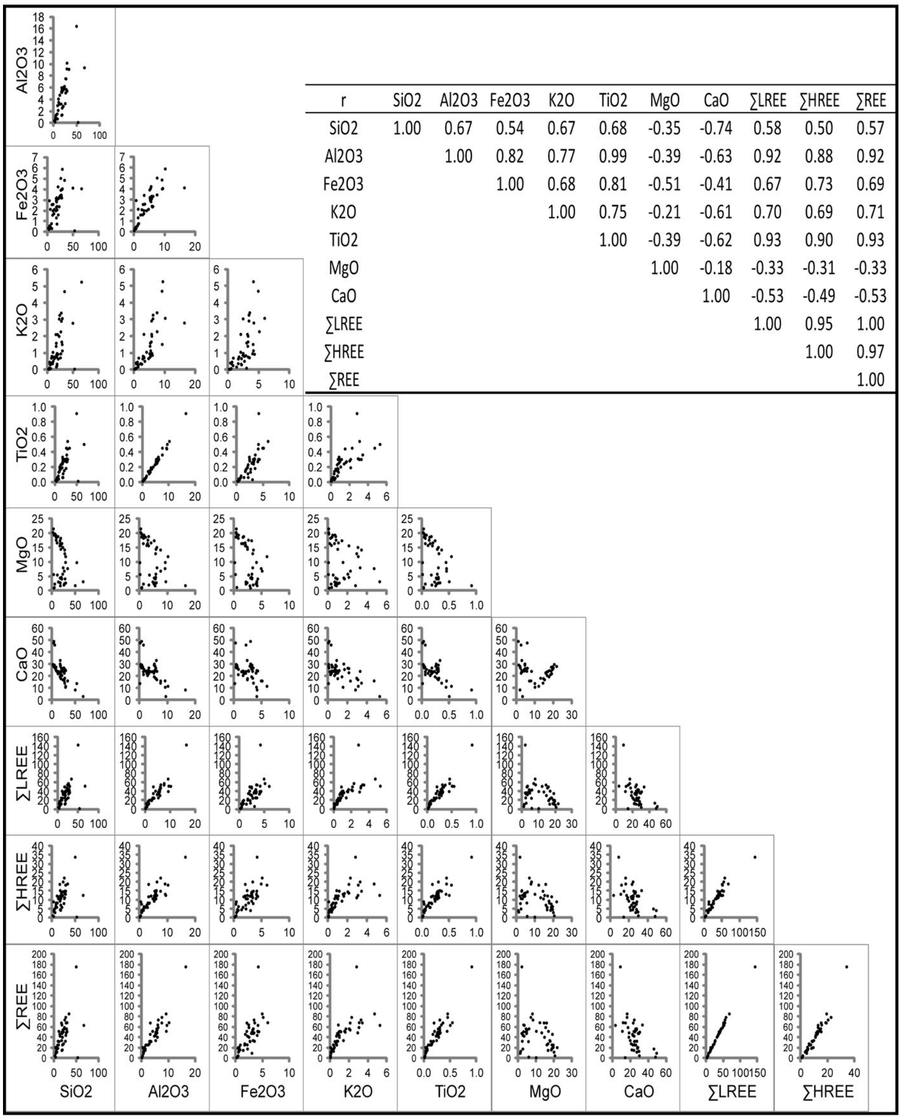
The absence of correlation between TOC and Na_2O, the weak correlation between TOT/C and Na_2O and the positive correlation between Na_2O and CaO (Table 2) are indicative of the association between Na and carbonates. The high correlation between TOT/S and Na_2O might suggest that Na is incorporated into sulfate minerals. The incorporation of Na into carbonates and sulfates is not expected. Na is usually associated with silicates [25] and/or pore water [7, 26]. The fact that Na_2O is not correlated with TOC but is strongly correlated with TOT/S might indicate that organic sulfur content is appreciably high.

The average TOT/C and TOC values are respectively 14.53% and 4.72% for oil shale, 12.53% and 3.21% for marl, and 6.52 and 2.51% for claystone (Table 1). TOT/C/TOC ratios for the respective units are 3.05, 3.90 and 2.60. These values signify that all rock units deposited in the basin are enriched in organic material. The fact that TOC content is very low in marl but high in oil shale implies that TOT/C is modified by carbonate in marl [6]. TOC abundances of oil shale, marl and claystone are high enough for oil production potential. The known limit value is 0.5% TOC and those with TOC > 2% are accepted to be a perfect source rock [27–29]. In general, high TOC values indicate reducing conditions whilst low TOC values point to oxidizing conditions. This general rule cannot explain the varying TOC values observed in the study area. Moreover, the TOT/S ratios of samples are very low. The average values of 0.80% for oil shale, 0.31% for marl and 0.48% for claystone reflect the oxic-dioxic character of the depositional environment. Considering that rocks were deposited in an oxic-dioxic environment, high organic carbon content is not a likely case. However, organic material might also be accumulated and preserved under oxic-anoxic conditions:

1. Biological productivity is high in the upper water column of the depositional environment.
2. Since dissolved oxygen and micronutrients such as phosphate and nitrates necessary for planktons are affected by seasonal conditions, short-term oxygen deficiency occurs in the water column, which results in a sudden mass extinction of all living organisms and thus a high amount of organic material is accumulated in the depositional environment.
3. Due to high sedimentation rate (clay and carbonate deposition), the accumulated organic material is covered and its contact with oxygen is disturbed. Thus organic material is protected from damage although the environment is of oxic character.

The gap between the maximum and minimum concentrations of major oxides is very high, which is attributed to variations in redox conditions and factors which supply elements to the depositional environment.

Based on major element distributions of different lithotypes two groups are differentiated. SiO_2, Al_2O_3, TiO_2, K_2O and Fe_2O_3, which increase from marl to oil shale and claystone, comprise the first group, and CaO and MgO, which decrease in the same order, make up the second group (Table 1). Examination of the correlation coefficients of major elements demonstrates that SiO_2, Al_2O_3, TiO_2, K_2O and Fe_2O_3 contents increasing from marl to oil shale and claystone are positively correlated. In this respect, a strong positive correlation between SiO_2 and Al_2O_3, K_2O, TiO_2 and Fe_2O_3 is noticeable (Fig. 2). This group is negatively correlated with CaO and MgO. There is a

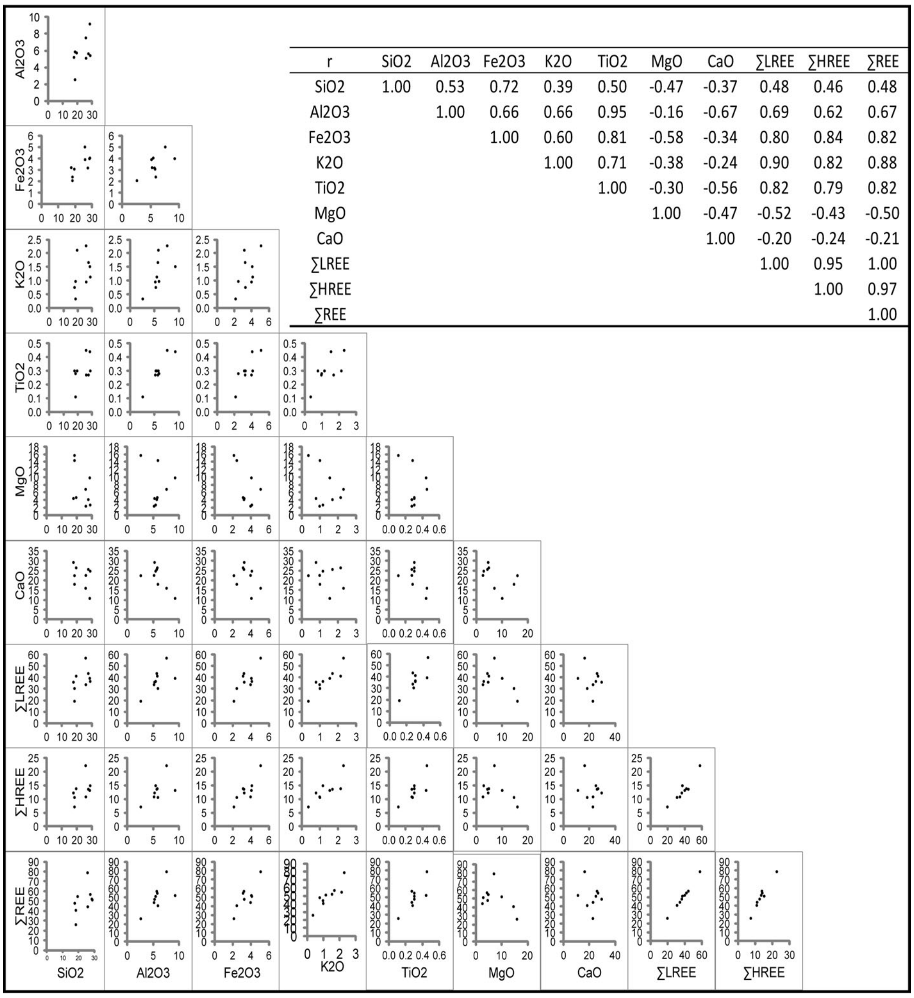


r	SiO2	Al2O3	Fe2O3	K2O	TiO2	MgO	CaO	∑LREE	∑HREE	∑REE
SiO2	1.00	0.67	0.54	0.67	0.68	-0.35	-0.74	0.58	0.50	0.57
Al2O3		1.00	0.82	0.77	0.99	-0.39	-0.63	0.92	0.88	0.92
Fe2O3			1.00	0.68	0.81	-0.51	-0.41	0.67	0.73	0.69
K2O				1.00	0.75	-0.21	-0.61	0.70	0.69	0.71
TiO2					1.00	-0.39	-0.62	0.93	0.90	0.93
MgO						1.00	-0.18	-0.33	-0.31	-0.33
CaO							1.00	-0.53	-0.49	-0.53
∑LREE								1.00	0.95	1.00
∑HREE									1.00	0.97
∑REE										1.00

Fig. 2. Correlation coefficients of REEs and major elements in all samples.

weak negative correlation between CaO and MgO which also show negative correlations with SiO_2, Al_2O_3, TiO_2, K_2O and Fe_2O_3, which represent compounds of detrital origin (Fig. 2). These results may indicate that Ca and Mg are of marine origin (associated with calcite and aragonite). The positive correlations between Si, Al, Ti and K are indicative of mixed clay assemblages such as kaolinite, illite, illite/smectite [7]. The high K content is attributed to the presence of illite.

The correlations established between the major elements in oil shales are very similar to those in the other rocks under study (Fig. 3). The correlation coefficients computed for oil shales are slightly lower than those of other rocks (e.g. coefficients calculated for SiO_2 vs. Fe_2O_3, Al_2O_3, TiO_2 and K_2O). In addition, the weak negative correlation between CaO and MgO in oil



r	SiO2	Al2O3	Fe2O3	K2O	TiO2	MgO	CaO	∑LREE	∑HREE	∑REE
SiO2	1.00	0.53	0.72	0.39	0.50	-0.47	-0.37	0.48	0.46	0.48
Al2O3		1.00	0.66	0.66	0.95	-0.16	-0.67	0.69	0.62	0.67
Fe2O3			1.00	0.60	0.81	-0.58	-0.34	0.80	0.84	0.82
K2O				1.00	0.71	-0.38	-0.24	0.90	0.82	0.88
TiO2					1.00	-0.30	-0.56	0.82	0.79	0.82
MgO						1.00	-0.47	-0.52	-0.43	-0.50
CaO							1.00	-0.20	-0.24	-0.21
∑LREE								1.00	0.95	1.00
∑HREE									1.00	0.97
∑REE										1.00

Fig. 3. Correlation coefficients of REEs and major elements in oil shales.

shales is absent in other rocks. This relation might imply that Ca and Mg may be derived from different sources. Mg with a detrital origin is known to be genetically related to clay minerals [6, 7, 30].

SiO_2 and Al_2O_3 contents of rocks are in the following order: claystone > oil shale > marl (Table 1). SiO_2/Al_2O_3 ratios are 3.80 in claystone, 3.96 in oil shale and 4.85 in marl and SiO_2 excess for these three lithologies is noticeable. SiO_2/Al_2O_3 ratios <1 indicate Al_2O_3 abundance and marine environment and clay enrichment whilst SiO_2/Al_2O_3 ratios >1 point to the abundance of detrital SiO_2 and particularly the presence of quartz [31]. Accordingly, SiO_2/Al_2O_3 ratios in these three rock groups are >1, indicating the input of detrital SiO_2 and principally the presence of quartz in the samples.

4.2. REE contents and origin by lithology

REE contents and geochemical trends of sedimentary rocks in the Dağhacılar region were used to determine genetic relations of these elements and redox conditions in the environment. Lithological characteristics influence REE concentrations.

Based on average values, REEs are more abundant in claystone (85.93 ppm), followed by oil shale (50.68 ppm) and marl (32.12 ppm) (Table 1). This comparison indicates that REE concentrations are controlled by clays rather than marl and organic material [32–36]. The wide range of REE concentrations in the examined samples is indicative of lithological variations of these rocks.

The order of REE abundances in rocks is also similarly observed in light rare earth elements / heavy rare earth elements (LREE/HREE) ratios. These ratios are 2.45–3.19 (avg 2.83) for oil shale, 1.55–3.80 (avg 2.85) for marl and 2.77–4.21 (avg 3.58) for claystone and the average of ratios increases from marl to oil shale to claystone (Table 1). The fact that the highest LREE/HREE ratio is found in claystone indicates that clay minerals are responsible for controlling LREEs rather than HREEs.

According to the results of correlation analysis of oil shale samples (Fig. 3), REEs show a strong positive correlation with the group of SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and K_2O, and a negative correlation with MgO and CaO. These relations imply that REEs are closely associated with clay minerals.

In order to examine the effect of organic material on REE enrichments, correlations were also computed for samples for which TOC analysis was made (Table 2). In this respect, correlations of LREEs and HREEs with major oxides are found to be similar to those for all the samples (Fig. 2). Like in case of correlation with TOT/C, HREEs strongly correlate with both TOC and TOT/S. Organic materials are also partly responsible for the abundance of REEs.

Correlation trends of REEs are generally similar to those of major oxides. However, the strong correlations of LREEs with elements in the clay fraction such as Si, Al, Fe, Ti, K and Na are noticeable. Furthermore, the correlation of P_2O_5 and CaO with REEs and HREEs is found to be stronger.

Correlations given in Table 2 demonstrate that 1) LREEs are chiefly controlled by clay minerals and partly by TOC and TOT/S and 2) HREEs are primarily controlled by P and CaO and also partly by TOC and TOT/S. According to [10], the correlation between HREEs and TOC is much stronger than that between HREEs and pyrite and apatite. Some researchers [6] state that LREEs are abundant in rocks with high clay and low TOC and pyrite contents, however, HREEs are accumulated in rocks with low clay and high TOC and pyrite contents.

For oil shales, a strong positive correlation was established between REEs and the group consisting of SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and K_2O, which represents the clay fraction. On the other hand, REEs negatively correlated with MgO and CaO (Fig. 3). The positive correlation between REEs and several major oxides such as SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and K_2O might indicate that clays and iron oxides-hydroxyls are primarily responsible for transportation and accumulation of these elements [14, 37, 38]. On the other hand, the negative correlations between REEs and CaO and MgO are consistent with the decrease in REE content with increasing carbonate abundance [6, 7].

4.3. REE enrichment in oil shales

REE contents of oil shales from the Dağhacılar region are lower than those of Post Archean Average Shale (PAAS), North American Shale Composite (NASC) and Upper Crust (UC) (Fig. 4). The undermost curve (the lowest abundance) belongs to Dağhacılar oil shale. Figure 4 illustrates three striking aspects: 1) regarding LREEs, the distance between the curves of similar environments (PAAS, NASC) and UC and the Dağhacılar oil shales is wider while the same distance for middle rare earth elements (MREE) and HREE is narrower. This may indicate that LREEs of Dağhacılar oil shales are lower than those of other shales, 2) including the studied oil shales, LREE > MREE > HREE for PAAS, NASC and UC, and 3) trends of all curves are conformable, indicating that REEs of all environments are represented by similar correlations.

The enrichment degree of REEs in oil shales was computed by the formula $EF = (El/Al)_{sample} / (El/Al)_{shale}$ (El: Element, Al: Aluminium) [39] and enrichment coefficients of PAAS, NASC, UC and Dağhacılar oil shales were compared. As seen from the histogram in Figure 4, Dağhacılar oil shales are enriched with respect to three standards (PAAS, NASC and UC). The depletion in LRRE (La, Ce, Pr, Nd) was observed with respect to only PAAS. Enrichments with respect to NASC and UC are 1.67–2.98-fold while those for PAAS are lower (1.04–1.28) (Fig. 4).

4.4. Redox conditions of depositional environment

In this section, REE contents of rocks were standardized with respect to PAAS and UC and redox conditions were examined. Anomalies of REE abundances in 9 oil shale samples and the average REE values of rocks are

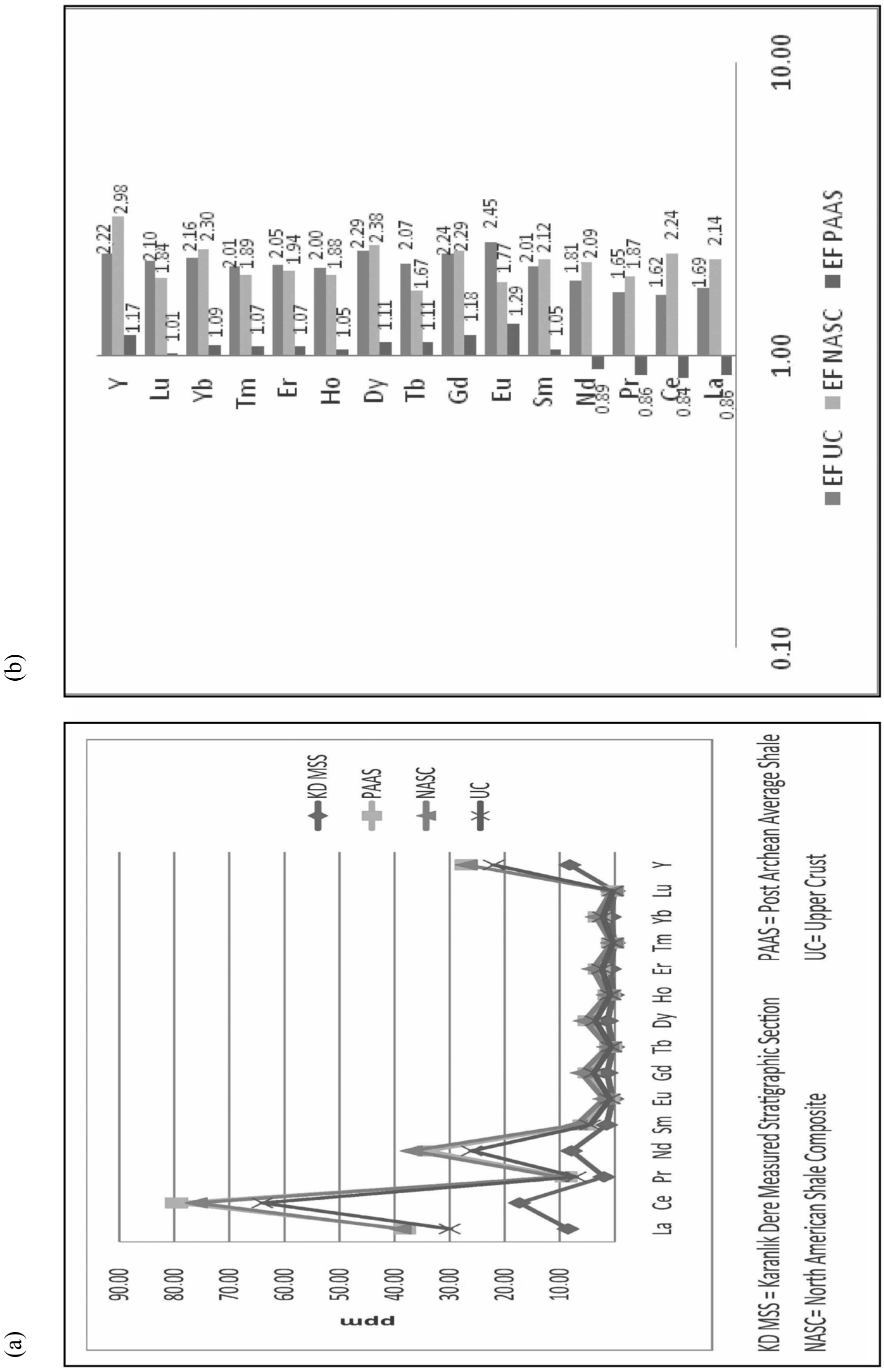
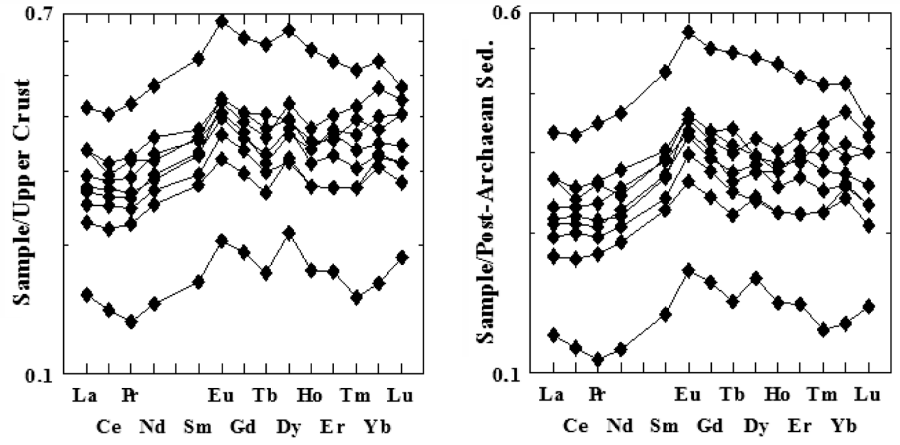


Fig. 4. REE abundances (a) and enrichment factors (b) of Kabalar oil shales with respect to other environments.

given in Figure 5. The positive Eu and slightly negative Ce anomalies in oil shales and other rocks are prominent in both figures.

Based on REE contents, the depositional environment of the Dağhacılar region is represented by oxic-anoxic conditions. The slightly negative Ce and Eu anomalies (Fig. 5) and Ce/Ce* and Eu/Eu* (Table 1) ratios indicate low oxic-anoxic (reducing) conditions [40, 41, 42]. These data are conformable to the TOT/C, TOC and TOT/S values of the environment.

(a) Oil shale samples



(b) Average values

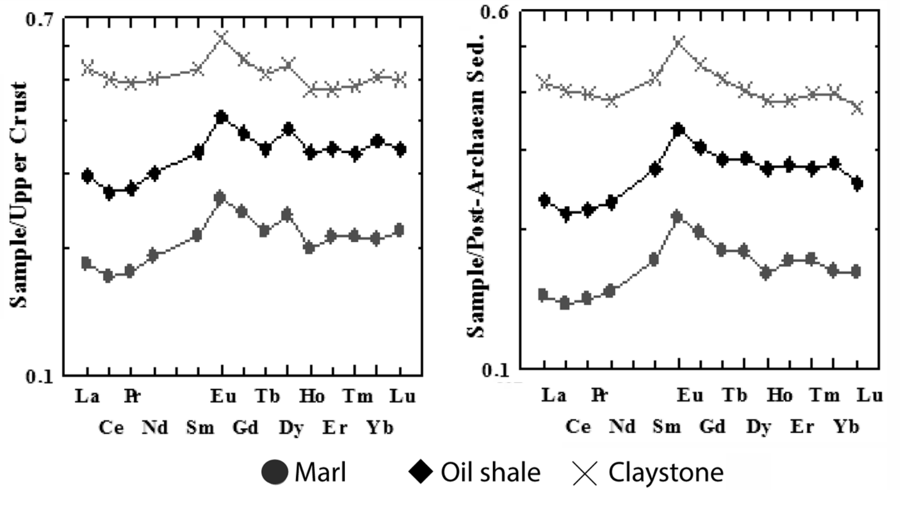


Fig. 5. Normalizations of REEs contents in oil shales (a) and other lithotypes (b) with respect to UC and PAAS.

5. Conclusions

1. All rock units deposited in the Dağhacılar region are enriched in organic material. The abundance of TOT/C and TOC in these units follows the order: oil shale > marl > claystone. The TOC content is 4.72% for oil shale, 3.21% for marl and 2.51% for claystone. These values are high enough for oil production.
2. Based on low TOT/S contents of oil shale, marl and claystone, it may be concluded that these units were deposited under oxic and anoxic conditions. Ce and Eu anomalies of rocks also imply that the environment was not of reducing character.
3. Although the depositional conditions were oxic-anoxic, TOC values are high. This interesting situation is explained by the following process: covering of organic material with protective layers, which was accumulated because of high biological productivity in the upper water column, high sedimentation rate and mass extinction arising from the deficiency of oxygen and micronutrients as a result of seasonal changes, in order to break off the contact with oxygen.
4. The abundance of major elements (e.g. SiO_2, Al_2O_3, TiO_2, K_2O and Fe_2O_3) follows the array: claystone > oil shale > marl. CaO and MgO abundances observe the order: marl > oil shale > claystone. In this respect, two different genetic groups are categorized: detrital and marine. Correlations between the elements also indicate the same groups. The first group consisting of SiO_2, Al_2O_3, TiO_2, K_2O and Fe_2O_3 is associated with clay minerals kaolinite, illite and illite/smectite. This group is negatively correlated with CaO and MgO. The second group represents marine origin. Although not observed in all rock samples, the weak negative correlation between CaO and MgO in oil shales might indicate that these elements are derived from different sources. In addition to its marine origin, Mg may also be genetically related to clay minerals. Ca and the major part of Mg are associated with carbonates.
5. TOT/C and TOC abundances follow the array: oil shale > marl > claystone and due to variations in redox conditions their concentrations range widely. TOT/C and TOC are positively correlated with the group representing the clay fraction and negatively correlated with CaO, MgO and MnO. Thus, TOT/C and TOC are associated with clays.
6. The abundance of SiO_2 in rocks follows the order: claystone > oil shale > marl, the SiO_2/Al_2O_3 ratio of these rocks is also high. These ratios are indicative of silica abundance and particularly the presence of quartz. The strong positive correlation of TOC-SiO_2 implies an organic source of silica and a detrital origin of quartz.
7. P_2O_5 is not correlated with TOC. However, its positive correlation with TOT/C points to that phosphate is not of organic origin and accumulates in apatite.

8. In addition to association with clays, the positive correlations of Fe_2O_3 with TOC and TOT/S indicate that iron is chiefly present in organic material and thus it may have two different sources. These data also imply the pyritization process.
9. Na_2O has a weak positive correlation with TOT/C, however, it is not correlated with TOC. In addition, Na_2O is positively correlated with CaO and TOT/S suggesting that Na is incorporated into carbonates and sulfates.
10. The abundance of REEs follows the order: claystone > oil shale > marl. REEs are negatively correlated with CaO and MgO and positively correlated with other major oxides indicating that REEs are controlled by clay minerals. Weak positive correlations of REEs with TOC and TOT/S might suggest that REEs are partly associated with organic material and pyrite. The highest LREE/HREE ratios are found in claystones. LREEs show strong positive correlations with elements in the clay fraction. This indicates that LREEs are controlled by clay minerals. The positive correlation of HREEs with P_2O_5 and CaO is much stronger than that of LREEs, implying that HREEs are controlled by P_2O_5 and CaO and also partly by TOC and TOT/S.
11. REE abundances of oil shales in the Dağhacılar region are lower than those of PAAS, NASC and UC. Comparisons of LREE, HREE and MREE contents reveal that the lowest LREE is found in Dağhacılar. For all environments (Dağhacılar, PAAS, NASC and UC) the concentration range follows the order: LREE > HREE > MREE.

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