



The REE Characteristics of Oil Shales in the Lower Eocene Celtek Formation (Yozgat, Turkey) and their Relation to Tectonic Provenance

YAVUZ PEHLIVANLI Berna*

Department of Geological Engineering, Bozok University, Yozgat 66900, Turkey

Abstract: The Lower Eocene Celtek Formation is located in the Sorgun district of the city of Yozgat in Turkey. In the study area, Paleozoic, Campanian-Maastrichtian, Eocene, Miocene and Quaternary units are exposed. The Celtek Formation is noteworthy with its coal and oil shale deposits. Samples were collected from one exposure (YC ÖSK) and two boreholes (SJ and Ç boreholes) at the facility operated by the Yeni Celtek Coal Management. Concentrations of REE in oil shales from these localities were determined using the ICP-MS technique. REE and total organic carbon (TOC) values of a total of 32 samples were compared with normalized REE contents of various environments. TOC contents of the samples ranged from 1.37wt% to 11.8wt% (mean 4.96wt%). The averages of all samples for the all normalized values show similar patterns. Normalized REE patterns are represented by the enrichment in the order of LREE>MREE>HREE and display negative Ce and positive Eu anomalies. Σ REE vs. TOC were compared. Σ REE vs. TOC showed a weak positive correlation, whereas Σ LREE vs. (M+HREE) and Σ LREE vs. Σ REE were positively correlated. Regarding tectonic provenance characteristics, the Celtek Formation oil shales were formed in microenvironments with physicochemical conditions changing in character from oxic to euxinic, representing a transitional terrestrial–marine environment.

Key words: rare earth element, geochemistry, Ce anomaly, Eu anomaly, tectonic provenance, Celtek Formation, oil shale, Sorgun (Yozgat), Turkey

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1 Introduction

REEs are generally used for the assessment of geochemical reactions taking place between wall rocks and surface and groundwaters (Elderfield et al., 1990; Smedley, 1991; Johannesson et al., 1999). REE patterns of most organic material-rich deposits are normalized to NASC.

During complex-forming reactions, REEs show chemical fractionation and adsorption effects and display a strongly mobile character in the global biochemical cycle. REE patterns of organic materials are distinguished as N (Normal-NREE), L (light-LREE), M (middle-MREE) and H (heavy-HREE) (Yudovich and Ketris, 2006). Therefore, since the paleoenvironment and the geological conditions under which organic materials are formed are quite different, in some organic materials heavy REEs are much more enriched than light REEs (Kosterin et al., 1963; Eskenazy, 1987; Eskenazy, 1999) whereas in some others light REE contents are dominant (Goodarzi, 1987; Dai et al., 2008). Studies show that HREEs attract organic material much more than LREEs and thus HREE enrichment is high (Querol et al., 1995; Eskenazy, 1999). The reason for the enrichment of MREE is the extraction of humic material (Eskenazy, 1999; Seredin and Shpirt,

1999). Different organic material types from different regions may show both depletion and enrichment in MREE (Felitsyna and Morad, 2002). REE geochemistry is controlled by organic material and these RE elements (Thurman, 1985; Viers et al., 1997). Metal-organic material complexes detectable in natural waters were modeled in various studies (Lead et al., 1998; Hummel, 2002). Normalized values of Upper Crust (UC_n) and North American Shale Component ($NASC_n$) are taken from Taylor and McLennan (1985).

Among REE, medium rare earth element (MREE) enrichment represents enrichment in Sm, Gd, Tb and Dy, whereas light rare earth element (LREE) enrichment indicates enrichment in La, Ce, Pr and Nd and heavy rare earth element (HREE) enrichment refers to enrichment in Ho, Er, Tm, Yb and Lu. La/Lu ratios are indicative of LREE or HREE enrichment, whereas Gd/La and Gd/Lu ratios indicate depletion or enrichment in MREE (Johannesson et al., 2004).

A variety of factors may result in the enrichment of HREE, LREE and MREE (Eskenazy, 1999). As such, the high affinity of HREE for organic materials may indicate the effect of seawater, since the HREE/LREE ratio is mostly 1 in shale-normalized REE contents (Elderfield and Greaves, 1982; Hoyle et al., 1984; De Baar et al., 1985). Nearly negative δ Ce anomalies are attributed to a marine effect. A negative δ Eu anomaly is most probably

* Corresponding author. E-mail: bernayavuz80@gmail.com

due to plants (Wang et al., 1986). MREE enrichment in acidic waters is very characteristic (Elderfield et al., 1990; Sholkovitz, 1995; Sholkovitz et al., 1999).

In nature, all REEs are generally of RE^{3+} state. Eu^{2+} and Ce^{4+} have different states. These changes are related to the variations in redox conditions of hydrothermal or metamorphic fluids such as T, P, pH, f_{O_2} and chemical composition (Sverjensky, 1984; Wood, 1990; Bau, 1991).

In this study, REE characteristics of oil shale samples (YC ÖSK, SJ and Ç borehole) collected from the Celtek Formation in the Sorgun district of the city of Yozgat. REE contents of oil shales, which are regarded as an important source of oil around the world, may be used to examine the geochemical conditions of the depositional environment (Carroll et al., 1992; Graham et al., 1993). For this reason, samples from the Celtek Formation oil shales (CFOS) with notable REE contents are important to investigate the physicochemical conditions of the basin, its depositional character and provenance relationships.

2 Stratigraphy

The study area is in the Sorgun district of the city of Yozgat and covers an area of about 1000 km². Paleozoic, Campanian-Maastrichtian, Eocene, Miocene and Quaternary units are exposed.

The Central Anatolian granitoids (Erler and Bayhan, 1993; Dönmez et al., 2005) are the oldest rock unit in the area. They are unconformably overlain by the lower Miocene Celtek Formation. The Celtek Formation is also unconformably overlain by the lower-middle Eocene Boğazköy Formation. Ophiolitic rocks of the İzmir-Ankara-Erzincan suture zone thrust over the Boğazköy Formation during the end of the Lutetian. All these units are covered by Neogene deposits (Figs. 1–2).

The Central Anatolian granitoids are unconformably overlain by the Celtek, Boğazköy and Kızılırmak Formations. The Celtek Formation is composed of sandstone, coal, oil shale, alternating lenticular sandstone

and mudstone (Cicioğlu, 1995). The borders of the formation with the overlying Boğazköy Formation and Neogene deposits are discordant. The Boğazköy Formation starts with a basal conglomerate and continues with volcanite interbedded sandstone, fossiliferous limestone, claystone, clayey limestone, marl, and a variety of volcanic rocks such as rhyolite, rhyolitic tuff, agglomerate, dacite, andesite and basalt. The Kızılırmak Formation is composed of, from bottom to top, terrestrial conglomerate, sandstone, siltstone, claystone, mudstone and limestone (Beyazpınar et al., 2015). It is covered by Plio-Quaternary units.

3 Material and Methods

Oil shale samples used in this study were collected from one exposure (YC ÖSK ($n=9$)) and two boreholes (SJ ($n=10$) and C ($n=10$) boreholes) at the facility operated by YeniCeltek Coal Management. Surface samples were systematically collected from measured stratigraphic sections. The samples were compared with Estonian, Jordanian and Utah oil shale samples ($n=3$) from which oil is economically produced. Also, the REE values of the samples were normalized to world average values such as Post Archean Average Shale (PAAS_n), North American Shale Composite (NASC_n), Upper Crust (UC_n), Average Shale (AS_n) and Chondrite (C_n) values. In order to better understand the element enrichment in the basin, CFOS rocks were separately analyzed. Sample preparation and microscopic studies were conducted at the laboratories of the Geology Department of the Bozok University and SEM-EDX determinations were made at the BILTEM laboratories of the same university. ICP-MS analysis was conducted at ACME laboratories (Canada), XRD analysis was carried out at MTA laboratories ($n=32$) and total organic carbon analysis was made by Turkish Petroleum Corporation (TPAO) laboratories. XRD analysis was conducted with Cu X-ray tube Philips Panalyticalbrand XRD device.

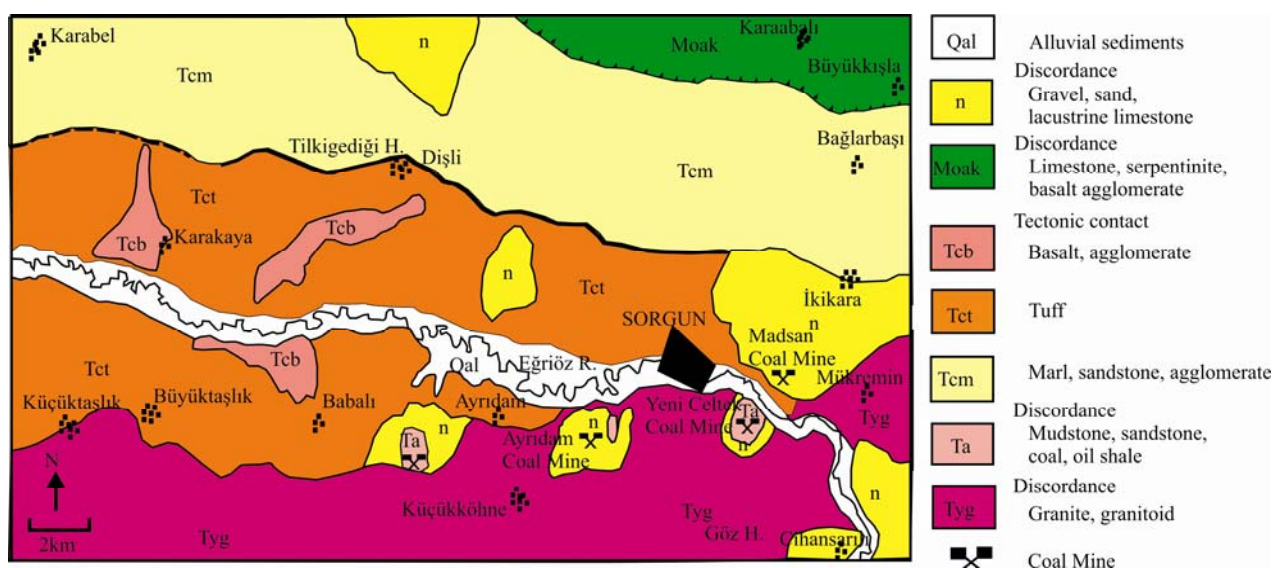


Fig. 1. Geological map of the study area (after Cicioğlu, 1995).

Age	Formation	Lithology	Description
Quaternary	Quaternary sediment		Sand, gravel storage
Pliocene	Cover Unit		Discordance Conglomerate, sandstone, mudstone
Middle Miocene	Kızıllırmak		Discordance Limestone, clayey-limestone, conglomerate, sandstone, siltstone, claystone, mudstone
Upper Cretaceous	Artova complex		Serpentine, mudstone, radiolarite, gabbro, diabase basalt, limestone, marble schist
	Dermik		Tectonic Contact Boyalı Member: volcanic intercalated conglomerate, sandstone, claystone, mudstone and clayey limestone Volcanic Member: Spilitic basalt, basaltic-andesitic lava and pyroclastic
Lower Middle Eocene	Bogazkoy		Tectonic Contact
			Agglomerate, basalt, andesite, dacite
			Clayey limestone
			Marl, fossiliferous limestone
Lower Middle Eocene	Celtek		Volcanic interbedded sandstone
			Conglomerate
			Discordance
Upper Cretaceous	Central Anatolian granitoids	Thickness 50m	Mudstone, lenticular sandstone, oil shale, coal, sandstone
			Discordance
Upper Cretaceous			Granite, granitoid, hornblende granite, monzonite, syenite, tonalite

Fig. 2. Generalized stratigraphic section of the Sorgun Basin (after Cicioğlu, 1995; Beyazpirinç et al., 2015).

4 Data and Results

4.1 Minerals

Using the whole rock analysis of 32 samples collected from the study area, mineral compositions were determined. Quartz, feldspar, dolomite, calcite, pyrite, gypsum, analcime and clay minerals are the major mineral phases in the samples (Table 1).

Results of XRD analysis show that quartz is the chief mineral in drill holes numbered C and in SJ and YC labeled surface samples. Feldspar and clay minerals accompany the quartz. In addition to these, dolomite, calcite, pyrite and gypsum are also recognized in varying amounts. According to the results of the XRD analysis, world oil shale samples contain quartz, dolomite, calcite, pyrite and analcime minerals.

In order to examine the crystal shape and size of minerals in the samples and their relation to other components, SEM and energy dispersive micro analysis (EDS/IXRF) studies were conducted on ten samples.

SEM-EDS analysis conducted on organic material (oil droplet) determined in the sample SJ.12 revealed C, O, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Ce, Eu, Fe and U elements at varying concentrations (Fig. 3). In organic material in particular, concentrations of Ti, Ce, Eu, Fe and U elements are noticeable (Figs. 4a–c and Fig. 5).

4.2 TOC content (wt%)

In order to determine the abundance and type of organic material present in the samples, pyrolysis analysis was carried out at the Turkish Petroleum Corporation (TPAO) laboratories. Some of this analysis was made using a Rock-Eval II type device. The analysis principle is based on heating a 100 mg powdered sample in a helium atmosphere for about 3 minutes. Both TOC and pyrolysis data can be obtained from the Rock-Eval II device which is integrated to a TOC module which automatically calculates the TOC value.

The TOC values for Celtek Formation oil shale are in the range of 1.37 to 11.8 (TOC_{mean}: 4.96). Assessment of organic carbon percentages with regard to bedrock classification yields very good to perfect rock character.

Studied oil shale samples are found to have similar source rock quality to standard ranges and oil shales from Estonia, Jordan and Utah where oil is produced (Table 2).

4.3 Inorganic element geochemistry

All elements that are soluble in water and can be adsorbed on organic and inorganic materials may be used to determine the depositional environment. These indicator elements may be retained in primary minerals or in organic material available in surrounding waters or they can be held in autogenic minerals during and just after sedimentation (Cody, 1971). In addition to trace element abundances, whole rock compositions and geochemical processes may also be used for determining the depositional environment.

All samples investigated in this study are collected from shale, limestone and marl which have high carbon content. For geochemical investigations in particular, shale samples were selected. Major, minor and rare earth element contents of oil shales of the Celtek Formation in the Sorgun Basin were determined using the ICP-MS method, and the results are shown in various tables and diagrams (Tables 3–5; Fig. 6).

The average element concentrations of samples are compared with those of oil shales from Estonia, Jordan and Utah where oil is produced (Figs. 5–6).

4.4 Element enrichments

Element enrichments of oil shales from the Celtek Formation in the Sorgun Basin were computed with the equation $[EF_{\text{element}} X = (X/Al)_{\text{sample}} / (X/Al)_{\text{standard}}$] of Brumsack (2006). If the calculated value is >1 , the sample is enriched with respect to the standard, whereas if the value is <1 then the sample is depleted. The average shale values are taken from Turekian and Wedepohl (1961).

Like upwelling environments and anoxic basins, the behavior of trace elements in organic carbon-rich sediments has been discussed in several studies (Brumsack, 1989; Calvert and Pedersen, 1993). Similar work was also carried out on old oil shales (Brumsack, 1980, 1986; Arthur et al., 1990). The enrichment of redox-sensitive elements reflects the depositional environment of TOC-rich sedimentary rocks and, therefore, they are used to investigate the conditions necessary for deposition (Brumsack, 1986; Hatch, and Leventhal, 1992; Piper,

1994; Yavuz Pehlivanlı et al., 2014). Organic carbon-rich rocks like those of the Cenomanian-Turonian boundary event (CTBE) are significantly enriched in sulfide occurrences and/or redox-sensitive trace elements (Brumsack, 1980; Arthur et al., 1990; Warning and Brumsack, 2000). TOC-rich recent sediments in the Black Sea (Brumsack, 1989; Kıratlı and Ergin, 1996) and Norwegian black shales are notably enriched in some trace elements (except for Co and Mo). Volgian and Early Berriasian black shales have accumulated trace elements such as V, Ag, Bi, Cd, Mo, Re, Sb, Tl, U, Co, Cu, Cr and Ni. Under reducing conditions, concentrations of these elements in sediments are quite high (Brumsack, 1980; Jacobs et al., 1985, 1987; Brumsack, 1989; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993). They are either bound to the organic material precipitating as free sulfides or precipitated as Fe-sulfides (Kremling, 1983; Jacobs et al., 1985).

Using the average shale data of Turekian and Wedepohl (1961), Mg, Fe, Si, K, Ti, Ca, Na, Cr, Pb, Zr, P, Sr, Rb, U, Ba, Cu, Ni, As, V, Zn, Sb, Co, Mo and Cd elements were evaluated. It can be seen in Table 6 that Si, Pb, U and As are enriched at almost all sampling sites. In well no. SJ; Si, K, Pb, Zr, Sr, Rb, U, Ba and As elements are enriched. Regarding average shales, uranium enrichments of Jordanian, Utah and Estonian shales are 36.19-, 3.66- and 3.11-fold, respectively. At all sampling sites of CFOS, U-enrichment is in the range of 1.19- to 153.76-fold with an average of 12.98-fold (Table 6).

4.5 REE content

The Σ REE contents of 29 samples collected from three different localities in the Çeltekk Formation together with reference values of Jordanian, Utah and Estonian shales are given in Table 7. The Σ REE values of the samples fall in the range of 119.61 to 2057.48 ppm with an average of 345.3 ppm. In a study by Wang et al. (2008), the total rare earth element content of

Table 1 XRD results of the samples (a=C, b=SJ, c=YC) in this study

Minerals	Quartz	Feldspar	Calcite	Dolomite	Pyrite	Kaolinite	Chloride	Mica-Ilite
C.1	X	X			X	X	X	X
C.2	X	X			X	X	X	X
C.3	X	X			X	X	X	X
C.4	X		X		X	X	X	X
C.5	X		X		X	X	X	X
C.6	X		X		X	X	X	X
C.7	X		X		X	X	X	X
C.8	X		X		X	X	X	X
C.9	X		X		X	X	X	X
C.10	X		X		X	X	X	X
C.11	X		X		X	X	X	X
C.12	X		X		X	X	X	X
C.13	X		X		X	X	X	X
C.14	X		X		X	X	X	X
C.15	X		X		X	X	X	X
C.16	X		X		X	X	X	X
C.17	X		X		X	X	X	X
C.18	X		X		X	X	X	X
C.19	X		X		X	X	X	X
C.20	X		X		X	X	X	X
C.21	X		X		X	X	X	X
C.22	X		X		X	X	X	X
C.23	X		X		X	X	X	X
C.24	X		X		X	X	X	X
C.25	X		X		X	X	X	X
C.26	X		X		X	X	X	X
C.27	X		X		X	X	X	X
YC.1	X		X		X	X	X	X
YC.2	X		X		X	X	X	X
YC.3	X		X		X	X	X	X
YC.4	X		X		X	X	X	X
YC.5	X		X		X	X	X	X
YC.6	X		X		X	X	X	X
YC.7	X		X		X	X	X	X
YC.8	X		X		X	X	X	X
YC.9	X		X		X	X	X	X
YC.10	X		X		X	X	X	X
YC.11	X		X		X	X	X	X
YC.12	X		X		X	X	X	X
YC.13	X		X		X	X	X	X
YC.14	X		X		X	X	X	X
YC.15	X		X		X	X	X	X
SJ.1	X		X		X	X	X	X
SJ.2	X		X		X	X	X	X
SJ.3	X		X		X	X	X	X
SJ.4	X		X		X	X	X	X
SJ.5	X		X		X	X	X	X
SJ.6	X		X		X	X	X	X
SJ.7	X		X		X	X	X	X
SJ.8	X		X		X	X	X	X
SJ.9	X		X		X	X	X	X
SJ.10	X		X		X	X	X	X
SJ.11	X		X		X	X	X	X
SJ.12	X		X		X	X	X	X

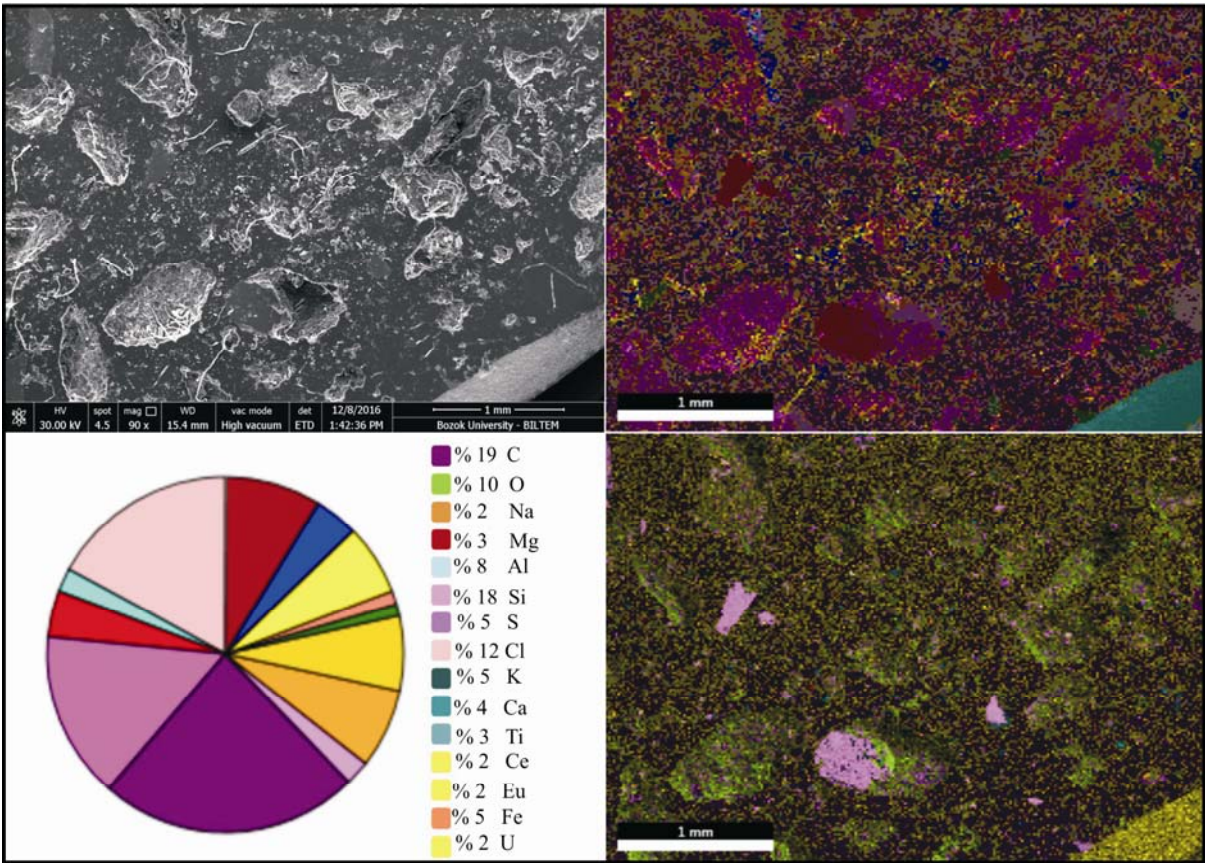


Fig. 3. Field survey with SEM of the SJ.12 sample showing significant enrichment of uranium.

Table 2 TOC content (wt%) of the samples in this study

Peters and Cassa (1994)		Tissot and Welte (1984)		Jarvie (1991)	
Corg (%)	Petroleum potential	Corg (%)	Source rock quality	Corg (%)	Source rock quality
0–0.5	Poor	0.1–0.5	Poor	0–0.5	Insufficient
0.5–1	Fair	0.5–1	Fair	0.5–1	Fair
1–2	Good	1–2	Good	>1	Adequate
2–4	Very good	2–10	Rich		
Sample No.	Corg (%)		Source rock quality		
C	1.97–16.17		Good-very good		
YC	2.14–14.85		Very good		
SJ	2.48–3.13		Very good		
Estonia	31.52		Very good		
Utah	3.56		Very good		
Jordan	16.71		Very good		

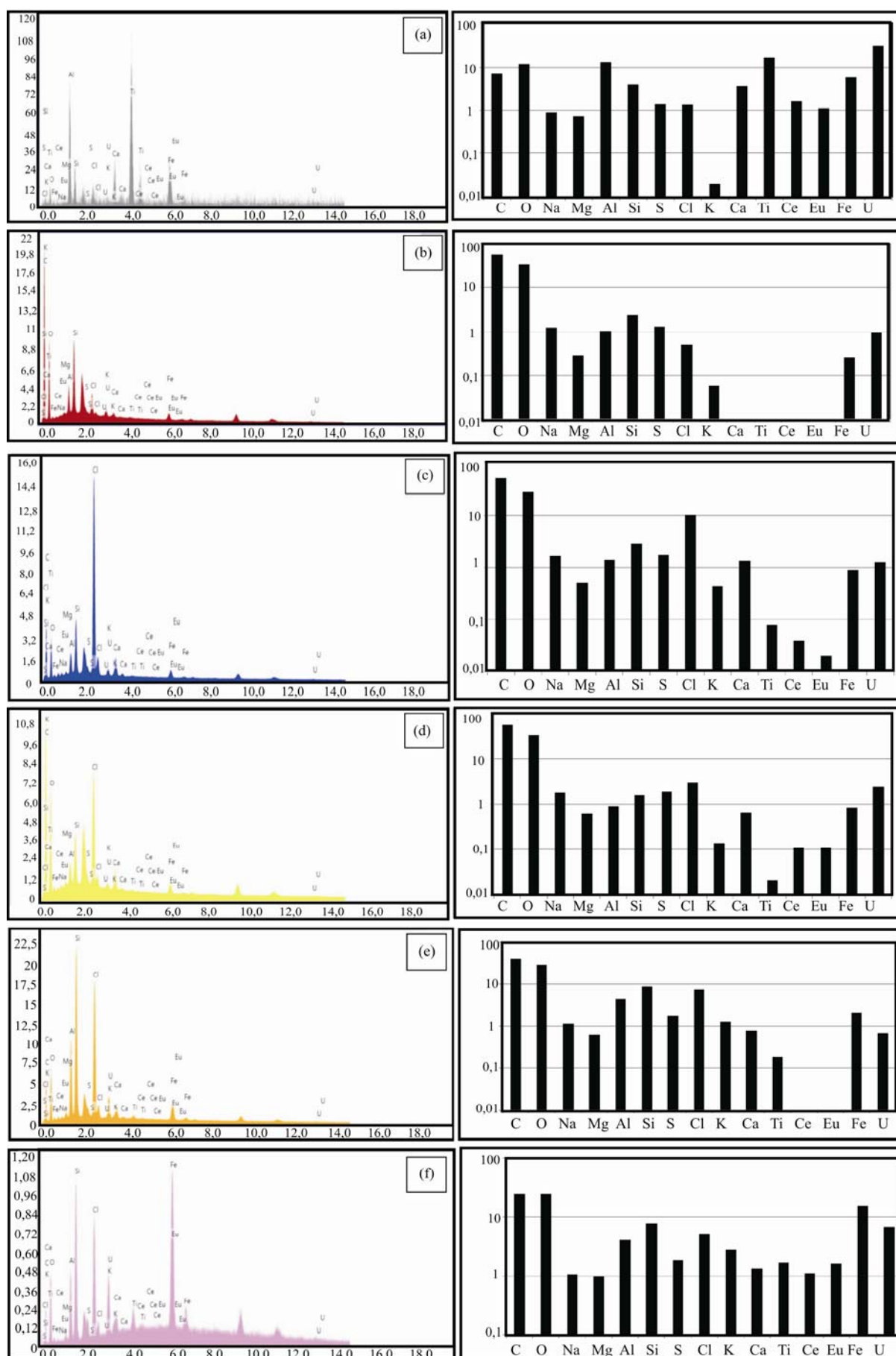
organic materials lies between 26.33 and 590.12 ppm. The average REE contents are 101 ppm for coals in the USA, 62.1 ppm for bituminous coals in the world (Finkelman,

1993) and 68.5 ppm for anthracites (Yudovich and Ketris 2006) and 137.9 ppm for Chinese coals (Dai et al., 2008). Furthermore, the average Σ REE of Estonian, Utah and Jordanian shales are 32.98, 75.44 and 50.37 ppm. The averages given in Table 8 are normalized with respect to standard values (Fig. 7). Normalized REE data for all the rocks are given in the relevant tables, and the normalized patterns are shown in the diagrams. The average Σ REE values of the samples are very low. In a study by Hannigan and Basu (1998), low REE values are attributed to the maturity level of the samples, and those with high REE content are identified as immature.

The averages of all samples for all normalized values show similar trends. Normalized values of MREE (Sm, Gd, Tb, Dy) show enrichment with regard to LREE (La, Ce, Pr, Nd) and HREE (Ho, Er, Tm, Yb, Lu). La/Lu ratios indicate if there is any LREE or HREE enrichment, whereas Gd/La and Gd/Lu ratios are indicative of MREE enrichment (Johannesson et al., 2004). MREE enrichment

Table 3 Average major oxide element concentration (wt%) of oil shale samples from the the Estonia-Utah-Jordan basins and samples in this study

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃
Estonia	10.11	2.23	0.99	0.65	13.44	0.05	1.21	0.14	0.09	0.01	0.004
Utah	26.83	5.57	3.48	6.23	24.52	1.21	2.46	0.18	0.05	0.03	0.004
Jordan	19.23	3.51	1.15	0.83	24.53	0.16	0.69	0.17	3.19	0.01	0.068
C avr. (n=10)	42.06	20.42	4.18	0.46	1.13	0.17	2.02	0.50	0.06	0.06	0.003
YC avr. (n=9)	46.38	22.22	6.25	0.93	0.65	0.19	2.42	0.48	0.10	0.11	0.005
SJ avr. (n=10)	59.94	13.71	4.63	1.28	4.73	1.13	3.91	0.52	0.10	0.06	0.005
Basin avr. (n=29)	49.46	18.79	5.02	0.89	2.17	0.50	2.78	0.50	0.08	0.08	0.004



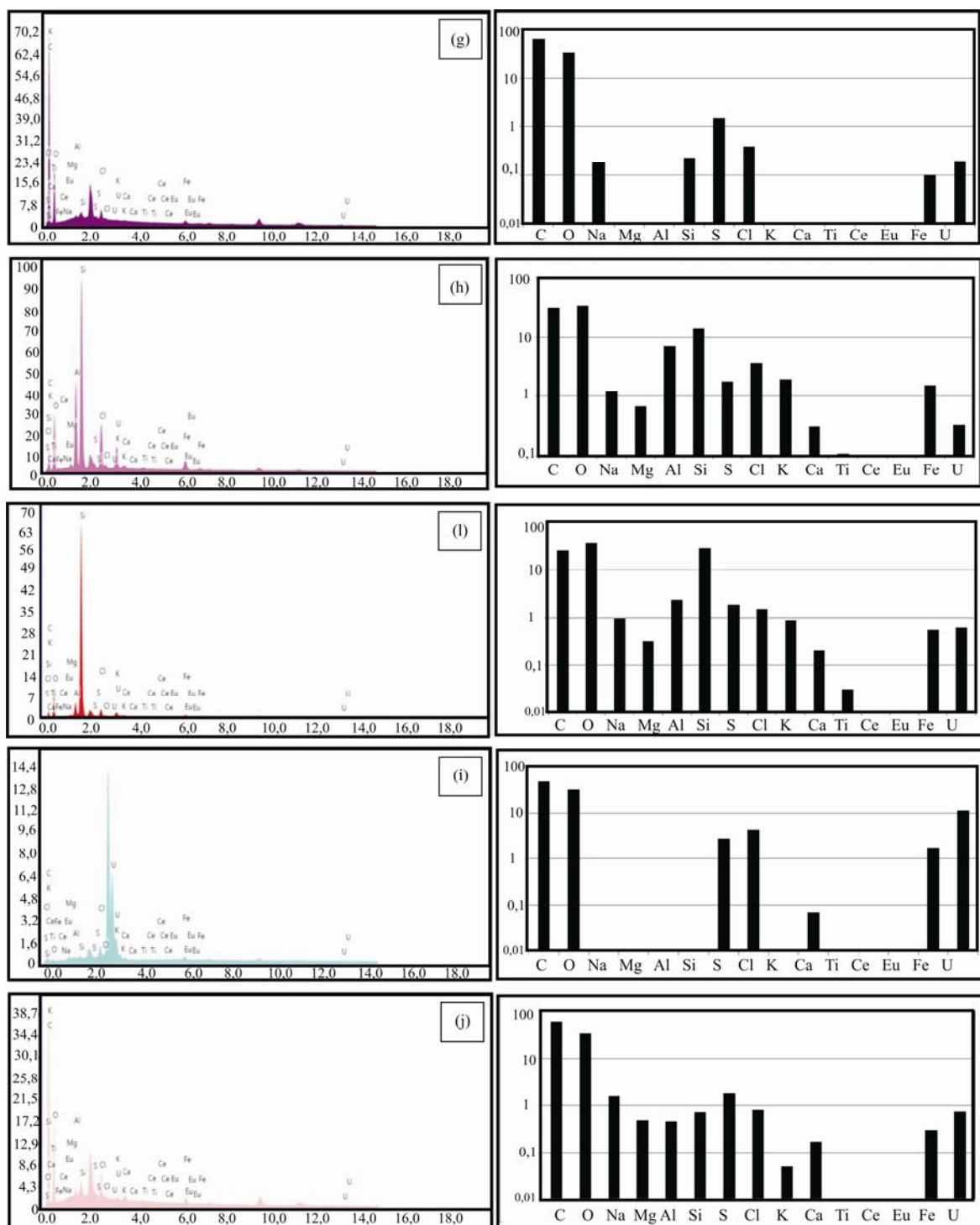


Fig. 4. Field analysis on 11 points of the SJ.12 sample showing significant enrichment of uranium with SEM-EDS.

Table 4 Average trace element concentration (ppm) of the oil shale samples from the Estonia-Utah-Jordan basins and the samples in this study

Samples	Ba	Sc	Co	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi
Estonia	77.0	2.0	3.2	0.8	1.5	0.9	2.6	22.0	0.9	239.6	0.2	2.5	1.7	20.0	18.7	33.8	1.6	3.5	15.4	5.0	9.9	4.1	0.1	0.1	0.1
Utah	588.0	4.0	17.3	3.3	5.2	1.1	4.3	71.8	0.9	1235.0	0.3	5.2	5.0	54.0	52.9	43.7	12.0	14.6	14.8	33.0	12.8	62.5	0.4	0.8	0.2
Jordan	53.0	5.0	4.9	0.7	2.9	0.9	3.1	14.2	0.9	751.5	0.2	2.0	31.1	297.0	9.3	38.5	103.1	94.9	6.6	924.0	230.3	6.8	150.3	1.7	0.1
C avr. (n=10)	724.1	7.1	10.6	22.5	25.1	5.0	18.2	142.9	4.5	228.8	1.0	63.0	45.6	74.1	34.5	187.0	3.3	18.7	104.1	100.5	7.9	28.6	0.3	0.8	2.7
YC avr. (n=9)	370.4	12.0	17.4	20.8	26.9	3.8	13.7	153.3	4.5	185.9	0.8	49.4	13.4	112.6	27.8	132.9	4.0	27.8	72.0	166.0	12.4	34.5	0.4	0.5	2.4
SJ avr. (n=10)	732.8	9.3	15.7	37.1	14.8	5.3	13.9	186.1	3.2	409.7	0.9	29.3	81.5	82.5	75.4	214.2	4.5	17.6	41.6	72.1	12.6	39.5	0.2	0.7	0.8
Basin avr. (n=29)	609.1	9.5	14.5	26.8	22.2	4.7	15.3	160.8	4.1	274.8	0.9	47.2	46.9	89.7	45.9	178.0	3.9	21.4	72.6	112.9	11.0	34.2	0.3	0.7	2.0

Table 5 Average REE element concentration (ppm) of the oil shale samples from the Estonia-Utah-Jordan basins and the samples in this study

Samples	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	ΣREE+Y
Estonia	7.80	7.30	12.30	1.59	6.30	1.14	0.26	1.22	0.20	1.01	0.20	0.63	0.08	0.66	0.09	32.98	40.78
Utah	10.60	17.40	30.80	3.51	13.30	2.47	0.47	2.36	0.32	2.03	0.35	1.20	0.15	0.93	0.15	75.44	86.04
Jordan	24.00	12.20	15.70	2.34	9.30	1.80	0.50	1.99	0.32	2.20	0.49	1.64	0.24	1.39	0.26	50.37	74.37
C avr. (n=10)	36.09	133.98	227.60	21.26	68.83	10.31	2.05	8.58	1.16	6.55	1.19	3.53	0.52	3.46	0.51	489.52	525.61
YC avr. (n=9)	23.94	83.24	142.60	14.14	47.13	7.66	1.55	6.17	0.81	4.53	0.84	2.41	0.36	2.30	0.35	314.10	338.05
SJ avr. (n=10)	25.92	58.76	98.58	10.86	38.41	6.70	1.44	5.84	0.82	4.61	0.87	2.49	0.35	2.23	0.34	232.29	258.21
Basin avr. (n=29)	28.81	92.30	156.73	15.46	51.61	8.24	1.69	6.89	0.93	5.25	0.97	2.82	0.41	2.68	0.40	346.38	375.19

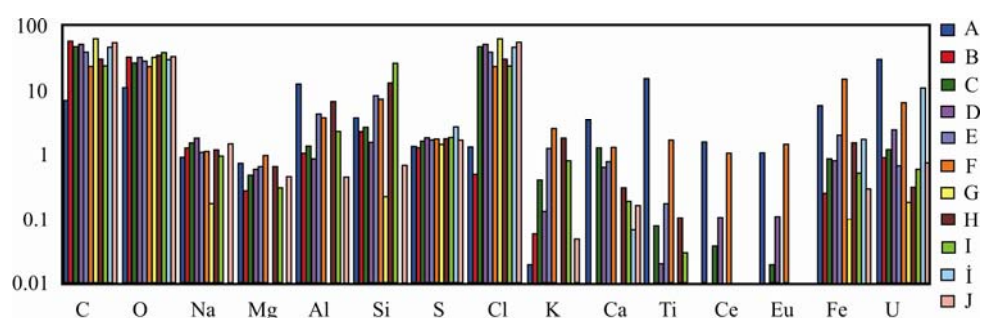


Fig. 5. Element content of the SJ.12 sample with SEM-EDS.

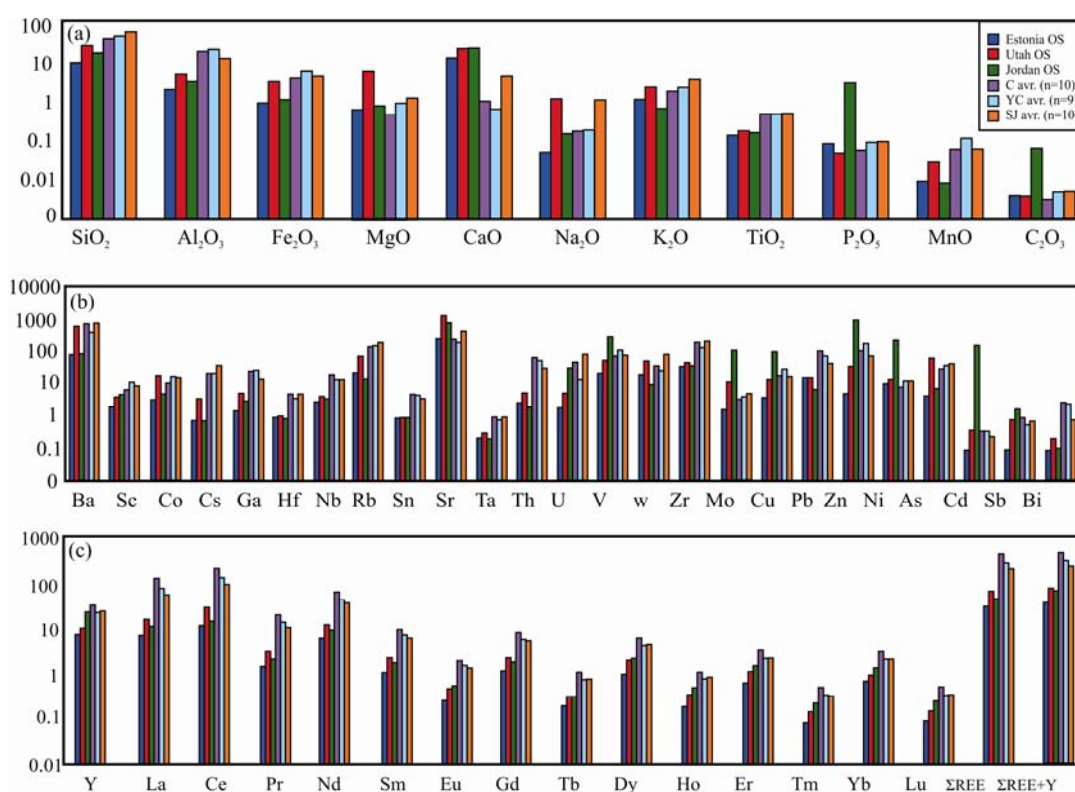


Fig. 6. Major element (a), trace element (b) and REE (c) contents of the oil shale samples from the Celtek Formation in the Sorgun Basin.

is very characteristic of acidic waters (Elderfield et al., 1990; Sholkovitz, 1995; Sholkovitz et al., 1999). Normalized REE patterns are generally in the order of LREE>MREE>HREE and show negative Ce and positive Eu anomalies.

ΣREE vs. TOC, ΣLREE vs. (M+HREE) and ΣLREE vs. ΣREE diagrams are displayed in Fig. 8. ΣREE vs. TOC shows a weak positive correlation, whereas the other two

diagrams are represented by strongly positive correlations.

4.6 Assessment of the depositional environment of oil shales of the Celtek Formation with the use of trace element contents

In order to have detailed information on provenance and paleogeography, the depositional basin of the source area and its tectonic relationships should be known and

understood. Tectonic conditions may be evaluated with mineralogical and geochemical data of the source rock. From the plate tectonic perspective, the origin of the source rock would be cratonic block, volcanic arc systems, collision belts and passive or rifted continental margins, active or orogenic belts and transform fault margins (Müller and Groves, 2000).

Major and trace element contents of samples from clastic sedimentary basins yield information on the tectonic and sedimentary conditions of the basin. The geotectonic conditions of the sediments could be resolved using the chemical characteristics of various magmatic rocks (Crook, 1974; Bhatia and Crook, 1986; Floyd and Leveridge, 1987; Roser and Korsch, 1988; McLennan et al., 1990; Burnett and Quirk, 2001; Zimmermann and Bahlburg, 2003; Armstrong-Altrin et al., 2004; Strnad and Mihaljevic, 2005; Campos Alvarez and Roser, 2007; Jafarzadeh and Hosseini-Barzi, 2008; Wu et al., 2018). For such discrimination, trace elements that are immobile at varying conditions such as La, Y, Th, Zr, Hf, Nb, Ti and Sc and their ratios are used (Taylor and McLennan, 1985; Bhatia and Crook, 1986) (Figs. 9–18; Table 9).

4.7 Provenance of the sediments

TiO₂ vs. Ni and Th/Co vs. La/Sc diagrams might indicate that the studied samples are the products of a magmatic provenance consisting of rocks with high silica content such as granite, gneiss, dacite or any type of acidic (felsic) magmatic rock. In order to determine the provenance and general characteristics of the depositional environment, several element ratios were used and among them the Th/U ratio is around 2.93, which is very close to the upper crustal average (Th/U=3.8). High Th/Sc and Zr/Sc ratios represent felsic material input from recycled sedimentary provenances (Oni et al., 2014). Enrichment of incompatible elements such as Th is indicative of a felsic source rather than a mafic source. In other words, a high Th/U value might show that a source rock had a felsic character. Al₂O₃/TiO₂ ratios are between 19 and 56, indicating that the source rock is granite, granodiorite, rhyolite, dacite or an aplite type felsic or acidic magmatic rock. The Th/Sc ratio of samples from the central part of the basin ranges from 1.7 to 22.17, implying a

Table 6 Element enrichment of the samples in this study according to world shale averages (after Turekian and Wedepohl, 1961)

Average shales	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
Estonia	0.558	1.771	0.994	4.388	2.560	1.342	29.461	0.262	5.219	1.432	3.803	5.414	1.065	3.114	0.900	0.527	0.987	2.138	1.043	0.357	0.407	1.142	0.986	1.017
Utah	0.670	6.797	1.399	4.662	2.083	0.691	21.519	2.538	2.008	0.741	0.846	11.172	1.392	3.667	2.751	0.880	0.511	13.047	1.127	0.943	1.447	2.471	2.960	1.809
Jordan	0.319	1.437	0.734	5.303	0.927	1.035	34.163	0.532	1.421	1.036	85.648	10.788	0.437	36.198	0.394	9.082	14.585	2.253	9.839	41.886	4.881	1.111	40.363	1078.770
C.5	0.747	0.236	0.424	2.899	0.845	0.735	0.619	0.313	2.530	1.657	0.309	0.731	1.023	3.637	0.890	0.264	0.081	1.105	0.400	0.669	0.165	0.508	0.083	0.275
C.8	2.269	0.296	1.333	3.241	0.939	0.594	2.395	0.325	2.975	1.468	0.491	1.477	1.090	5.679	1.211	0.441	0.172	3.819	0.616	0.843	0.525	0.975	0.298	0.438
C.10	0.265	0.230	0.704	2.073	0.536	0.524	0.162	0.100	3.176	0.764	0.553	0.584	0.811	4.162	0.516	0.457	0.184	2.425	0.496	1.426	0.376	0.645	0.154	0.672
C.12	1.187	0.174	0.545	2.148	0.566	0.524	0.124	0.090	2.462	0.767	0.428	0.565	0.792	2.654	0.606	0.317	0.112	1.981	0.470	1.410	0.320	0.495	0.081	0.458
C.19	0.369	0.147	0.433	2.096	0.571	0.606	0.079	0.074	3.014	0.901	0.199	0.519	0.807	2.352	0.596	0.293	0.113	2.117	0.463	0.573	0.213	0.536	0.064	0.213
C.22	0.058	0.128	0.409	2.894	0.775	0.825	0.068	0.174	3.487	2.079	0.194	0.620	0.938	2.924	0.996	0.280	0.124	1.712	0.461	1.327	0.363	0.635	0.113	0.389
C.28	0.035	0.071	0.136	1.411	0.220	0.442	0.062	0.022	2.841	0.423	0.145	0.358	0.673	9.003	0.214	0.343	0.011	0.276	0.208	0.133	0.342	0.042	0.199	0.070
C.29	0.095	0.067	0.948	1.266	0.121	0.218	0.167	0.020	19.686	0.325	0.722	0.736	0.371	85.778	7.343	0.147	0.110	3.991	0.891	2.223	1.974	0.522	1.065	2.146
C.32	0.065	0.071	0.408	1.403	0.247	0.485	0.094	0.020	2.883	0.603	0.055	0.402	0.659	5.802	0.215	0.118	0.031	1.861	0.318	0.287	0.293	0.232	0.328	0.147
C.33b	0.038	0.064	0.162	1.372	0.180	0.379	0.065	0.016	3.103	0.296	0.096	0.344	0.535	2.872	0.178	0.260	0.033	0.294	0.325	0.190	0.138	0.155	0.267	0.172
YC.2	0.050	0.078	0.462	1.443	0.207	0.398	0.069	0.021	2.921	0.323	0.167	0.271	0.567	4.604	0.205	0.359	0.045	1.775	0.438	2.167	0.358	0.773	0.695	0.671
YC.5	2.864	0.322	1.225	2.033	0.515	0.597	0.321	0.057	2.766	0.884	0.508	0.501	0.738	2.182	0.548	0.258	0.091	0.968	0.461	0.709	0.197	0.503	0.067	0.247
YC.6	0.481	0.157	0.390	2.097	0.537	0.561	0.107	0.055	2.622	0.818	0.405	0.468	0.791	2.916	0.539	0.318	0.127	1.305	0.475	0.752	0.260	0.551	0.112	0.325
YC.7	0.184	0.191	0.524	2.280	0.592	0.547	0.149	0.080	2.535	0.867	0.649	0.565	0.816	3.014	0.608	0.425	0.115	1.653	0.492	2.137	0.198	0.994	0.142	0.991
YC.10	0.356	0.281	0.517	1.891	0.527	0.411	0.136	0.110	2.338	0.386	0.578	0.323	0.721	1.438	0.364	0.621	0.205	1.665	0.728	0.592	0.289	0.768	0.157	0.206
YC.12	0.564	0.315	0.738	2.442	0.561	0.387	0.170	0.076	2.169	0.460	0.427	0.484	0.804	1.954	0.466	0.389	0.148	2.629	0.685	0.705	0.203	0.557	0.325	0.254
YC.13	0.839	0.259	0.632	1.834	0.513	0.387	0.122	0.094	1.915	0.399	0.318	0.381	0.745	2.050	0.370	0.452	0.122	2.804	0.676	0.684	0.212	0.423	0.284	0.212
YC.14	0.645	0.349	0.561	2.149	0.589	0.499	0.122	0.072	2.373	0.451	0.285	0.418	0.792	1.694	0.415	0.508	0.133	1.617	0.733	1.828	0.218	0.426	0.184	0.326
YC.15	0.167	0.345	0.701	2.098	0.591	0.440	0.129	0.131	2.165	0.418	0.506	0.428	0.817	5.669	0.409	0.589	0.211	1.520	0.739	0.513	0.090	1.225	0.117	0.564
SI.2	0.614	0.525	0.653	4.686	1.425	0.844	3.158	1.106	1.487	1.603	0.698	1.670	1.368	1.782	1.937	0.315	0.326	1.120	0.526	0.445	0.332	0.648	0.057	0.207
SI.4	3.229	1.324	1.267	5.414	1.970	0.700	7.917	0.250	4.734	3.239	0.745	2.381	2.254	24.853	1.285	0.425	0.216	1.207	0.761	1.311	0.455	1.338	0.047	0.284
SI.6	0.681	0.819	0.785	3.923	1.350	0.892	1.824	1.583	2.509	1.486	1.032	1.494	1.547	23.097	1.646	0.446	0.300	2.443	0.836	1.046	0.276	0.882	0.009	0.345
SI.8	1.624	0.735	0.938	3.781	1.109	1.079	7.071	2.643	2.855	1.852	1.394	3.851	1.208	3.129	1.574	0.225	0.182	1.933	0.739	0.609	0.526	0.997	0.011	0.439
SI.10	0.154	0.488	1.088	3.017	0.962	0.727	0.215	0.116	3.246	0.980	0.349	0.901	1.465	9.620	0.689	0.619	0.331	6.899	0.733	1.957	0.498	1.116	0.476	1.246
SI.12	0.073	0.369	0.547	3.176	0.965	0.724	0.166	0.184	2.421	1.089	0.275	0.901	1.179	153.767	0.742	0.660	0.169	6.877	0.707	0.818	1.885	0.642	3.221	0.589
SI.14	0.091	0.307	0.295	5.969	1.540	0.661	0.119	1.027	1.188	1.412	0.384	1.363	1.490	5.323	1.666	0.137	0.071	4.867	0.407	0.363	0.328	0.810	0.067	0.185
SI.16	0.182	0.432	1.047	4.803	1.272	0.924	0.129	0.625	1.163	1.831	0.276	1.082	1.499	1.257	1.107	0.300	0.094	3.373	0.767	0.536	0.591	0.554	0.040	0.166
SI.19	0.227	0.466	0.586	3.776	1.621	0.884	0.184	0.881	1.512	1.549	1.089	1.581	1.669	2.112	2.127	0.319	0.150	1.789	0.622	0.629	0.245	0.629	0.017	0.138
SI.22	0.173	0.539	0.548	4.884	1.547	0.711	0.166	1.612	1.316	1.373	0.784	1.566	1.360	1.190	2.044	0.200	0.066	1.742	0.379	0.530	0.280	0.612	0.010	0.157

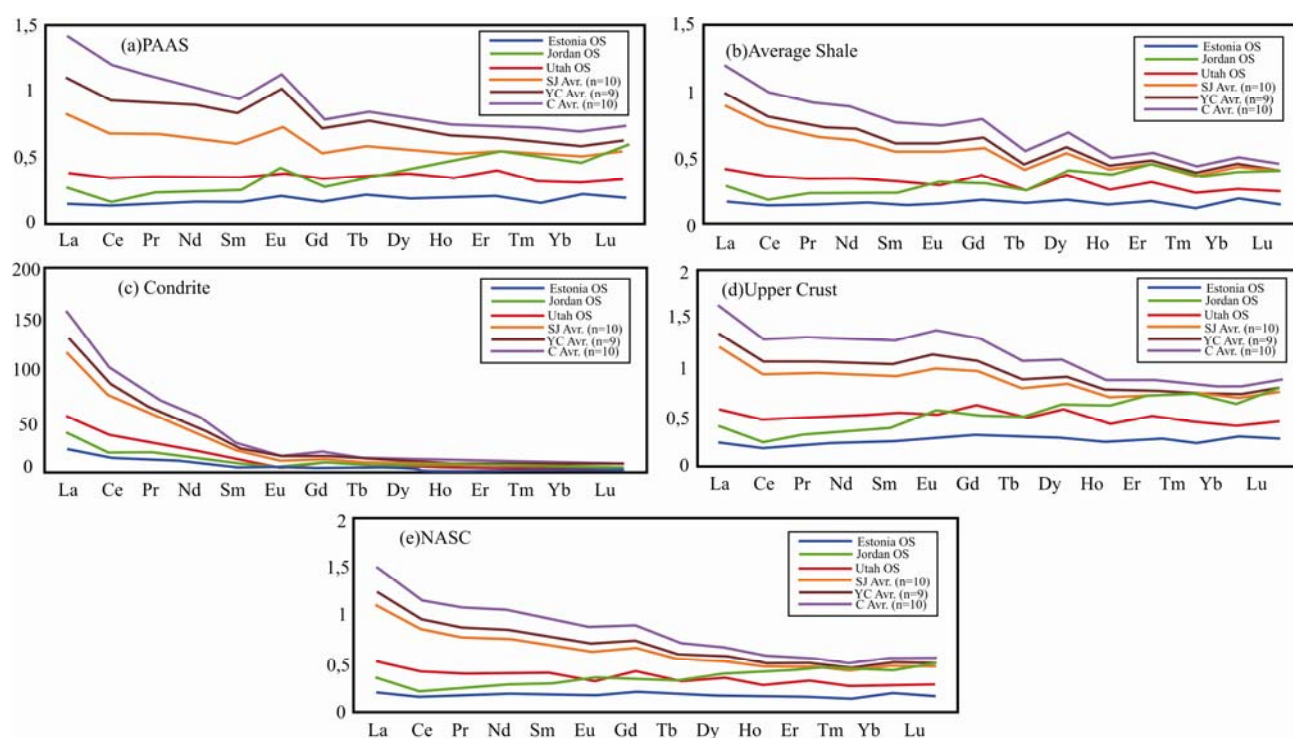


Fig. 7. REE trends normalized to (a) Post Archean Average Shale (PAAS_n), (b) average Shale (AS_n), (c) chondrite (C_n), (d) upper Crust (UC_n) and (e) North American Shale Composite (NASC_n).

Table 7 Σ REE and max-min change intervals of samples discussed in this study

Samples	Σ REE (ppm)	Max (ppm)	Min (ppm)
Estonia	32,98	-	-
Utah	75,44	-	-
Jordan	50,37	-	-
C avr. (n=10)	489,52	2057,48	206,94
YC avr. (n=9)	314,10	587,26	253,91
SJ avr. (n=10)	232,29	548,05	119,61
Basin avr. (n=29)	345,30	2057,48	119,61

Table 8 World average REE reference values (ppm)

REE	PAAS (mean)	Average shale	PAAS	Chondrite	Upper crust	NASC
La	44.56	41.00	38.20	0.31	30.00	33.04
Ce	88.25	83.00	79.60	0.81	64.00	70.55
Pr	10.15	10.10	8.83	0.12	7.10	8.70
Nd	37.32	38.00	33.90	0.60	26.00	31.76
Sm	6.88	7.50	5.55	0.20	4.50	5.99
Eu	1.22	1.61	1.08	0.07	0.88	1.38
Tb	6.88	6.35	4.66	0.26	3.80	5.50
Gd	0.89	1.23	0.77	0.05	0.64	0.94
Dy	5.33	5.50	4.66	0.32	3.50	5.54
Ho	1.05	1.34	0.99	0.07	0.80	1.16
Er	3.08	3.75	2.85	0.21	2.30	3.52
Tm	0.45	0.63	0.41	0.03	0.33	0.53
Yb	3.01	3.53	2.86	0.21	2.20	3.15
Lu	0.44	0.61	0.43	0.03	0.32	0.49

felsic type magmatic provenance. Th/Co ratios fall in the range of 0.98 to 20, which shows that the source rock was a sedimentary rock that was formed through the weathering of felsic or acidic type magmatic rocks such as granite (Figs. 14–18). Regarding tectonic setting, the Th/Sc vs. Zr/Sc diagram of McLennan et al. (1993) confirms input

from the zone of sediment recycling in the upper crust (Fig. 19).

5 Discussion

Since oil shales are formed in sedimentary rocks, the assessment of their rare earth element abundances is primarily important for understanding the geochemical character of depositional setting (Haskin and Gehl, 1962; Vine and Tourtelot, 1970; Huyck, 1990; Yudovich and Ketris, 1994; Hannigan and Basu, 1998). Some of the issues discussed in these studies include the role of various minerals in REE fractionation in oil shales, correlation between sedimentation rate and REE content and redox potential of the depositional environment.

Because of increasing energy demand and consumption rate, alternative energy resources are needed. For example, China, which is one of the energy-poor countries in the world, imported 163 million tons of crude oil in 2007 and 179 million tons in 2008. Since China does not have significant oil resources, coupled with the rapid increase in oil price, the energy demand of China has increased. It is noticeable that China has large reserves of oil shales, which are one of the alternative energy sources. Cenozoic oil shales in the Huadian (Liu et al., 2009) and Fushun (Qian et al., 2003) fields and Cretaceous bituminous shales in the Songliao Basin (Wang et al., 2008) were formed in lacustrine environments. Recent studies revealed the presence of new oil shale zones of marine origin around the Changshe Mountain in northern Tibet (Fu et al., 2011). In particular, rare earth element content in coal and oil shales have been a focus of attention

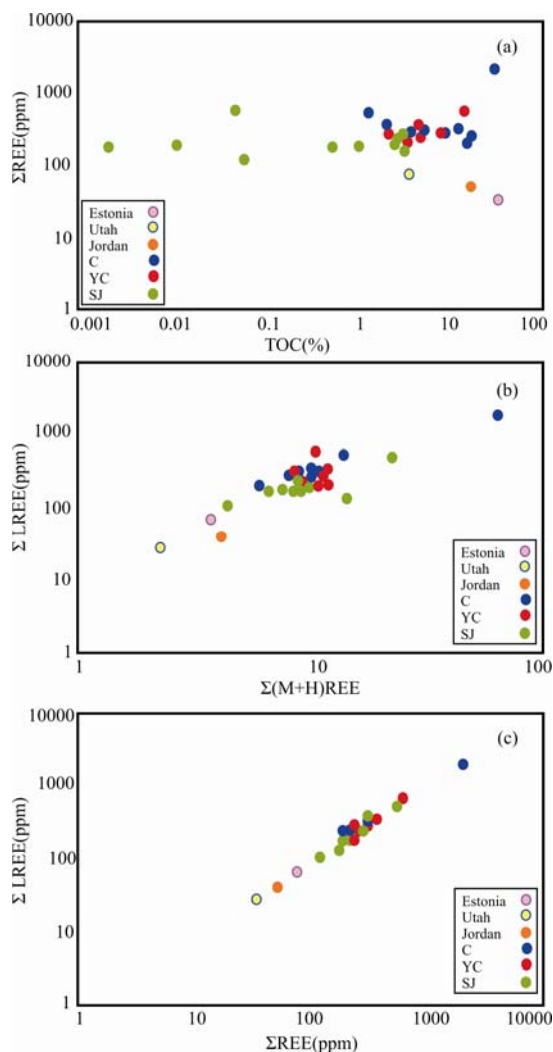


Fig. 8. (a) Diagram of ΣREE vs. TOC; (b) diagram of $\Sigma(\text{M+H})\text{REE}$ (Eu, Gd, Tb, Yb, Lu) vs. ΣLREE (La, Ce, Nd, Sm); (c) diagram of ΣLREE vs. ΣREE of the Estonia-Utah-Jordan oil shale samples and samples of the Celtek Formation in Sorgun Basin.

(Rantitsch et al., 2003; Wang et al., 2008). Therefore, a number of studies were conducted on the REE geochemistry of various shales (Condie, 1991; Dai et al., 2008; Wang et al., 2008; Ketris and Yudovich, 2009).

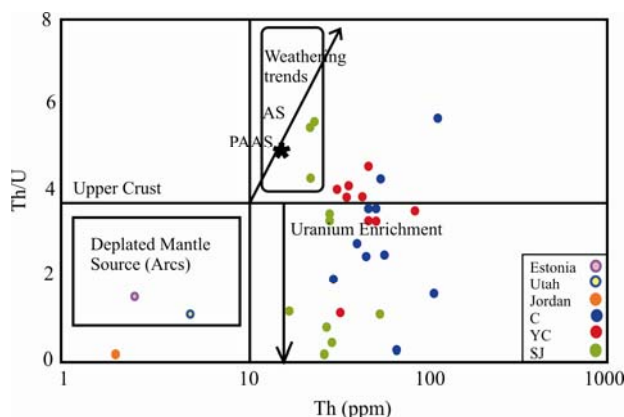
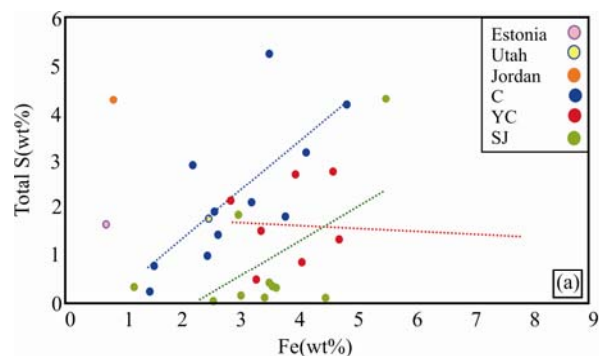


Fig. 9. Th-Th/U chart of Estonia-Utah-Jordan oil shale samples and samples of the Celtek Formation in Sorgun Basin. The weathering trend indicates uranium enrichment, while the arrow direction indicates uranium consumption.

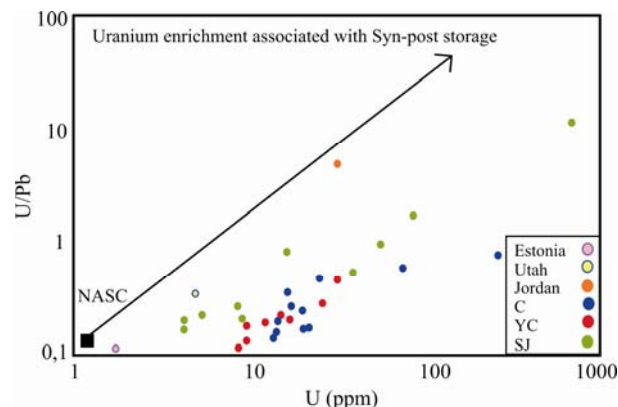


Fig. 10. The trend of uranium enrichment associated with syn-post storage in the U/Pb graph versus U of Estonia-Utah-Jordan samples and samples of the Celtek Formation in Sorgun Basin (after Lev et al., 2000).

It is known that particularly organic carbon-rich units accumulate REE much more than any other rock (Condie, 1991; Reynard et al., 1999; Rantitsch et al., 2003; Qi et al., 2007; Dai et al., 2008; Wang et al., 2008; Ketris and Yudovich, 2009). Heavy rare earth elements (HREE), which are highly mobile, are enriched in the organic material (Grandjean-Lécuyer et al., 1993; Kidder and Eddy-Dilek, 1994).

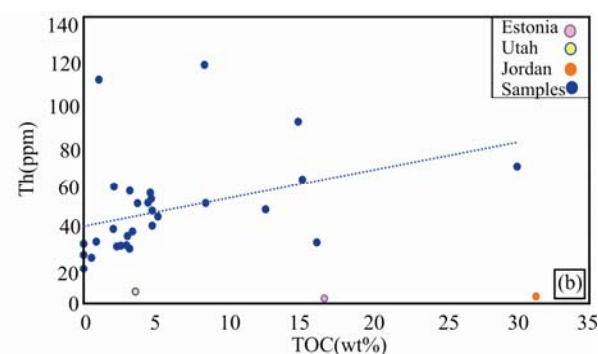


Fig. 11. (a) Relation of total S concentration and Fe content of oil shales samples from Estonia-Utah-Jordan and the Celtek Formation in Sorgun Basin; (b) diagram showing a weak positive correlation between Th and TOC of oil shales samples from Estonia-Utah-Jordan and the Celtek Formation in Sorgun Basin.

Table 9 Ratios of REEs normalized to chondrite, upper crust and NASC of the oil shale samples from the Estonia-Utah-Jordan basins and samples in this study

Chondrite	La/Sm	La/Yb	Gd/Yb	La/Pr	Gd/Dy	Ce/Yb	Lu/La	ΣREE (ppm)	LREE (ppm)	HREE (ppm)	MREE (ppm)	Eu/Eu*	Ce/Ce*
C.5	6.49	24.86	1.95	2.04	1.82	16.71	0.04	686.03	613.78	72.26	89.79	0.90	0.68
C.8	5.54	16.30	1.93	1.93	1.60	11.07	0.05	543.76	460.13	83.63	89.92	0.89	0.71
C.10	6.54	22.21	2.04	2.14	1.68	13.76	0.05	708.95	618.91	90.04	103.47	0.84	0.71
C.12	6.82	24.25	2.24	2.15	1.64	15.64	0.04	740.73	650.09	90.63	104.79	0.88	0.68
C.19	7.15	30.15	2.43	2.19	1.86	19.05	0.04	762.69	681.76	80.93	100.29	0.87	0.69
C.22	7.80	24.85	1.95	2.29	1.61	14.97	0.04	614.18	542.14	72.05	79.61	0.84	0.66
C.28	9.13	39.99	2.46	2.51	1.74	21.26	0.03	1242.52	1132.65	109.87	140.10	0.76	0.63
C.29	8.20	23.91	2.01	2.31	1.47	17.64	0.04	4432.32	3903.50	528.81	555.41	1.03	0.63
C.32	9.27	29.56	2.06	2.55	1.61	14.93	0.03	478.32	423.97	54.35	58.52	0.73	0.65
C.33b	9.70	27.62	1.62	2.71	1.40	12.44	0.03	679.11	601.00	78.11	80.41	0.66	0.58
YC.2	8.67	72.36	3.99	2.34	2.27	47.59	0.01	1240.62	1169.34	71.27	123.16	0.92	0.59
YC.5	7.89	22.49	1.86	2.43	1.45	12.72	0.04	631.51	548.55	82.95	86.86	0.80	0.67
YC.6	6.33	25.60	2.41	2.06	1.68	17.20	0.04	795.12	702.51	92.60	114.81	0.91	0.68
YC.7	6.67	26.95	2.22	2.18	1.80	16.94	0.04	652.26	581.71	70.55	87.55	0.86	0.64
YC.10	5.12	14.58	1.82	1.99	1.48	9.97	0.07	595.40	495.30	100.10	103.40	0.91	0.66
YC.12	5.86	22.13	2.31	2.10	1.54	14.51	0.05	588.34	509.08	79.26	92.52	0.89	0.69
YC.13	6.26	20.41	2.12	2.07	1.56	12.88	0.05	682.28	586.12	96.16	106.63	0.85	0.73
YC.14	5.51	17.31	2.00	2.00	1.54	11.85	0.06	602.18	511.13	91.05	99.25	0.91	0.66
YC.15	5.48	14.84	1.99	1.94	1.61	9.97	0.07	603.93	499.17	104.76	106.07	0.89	0.76
SJ.2	4.92	16.86	1.94	1.93	1.66	10.83	0.06	443.57	377.72	65.85	75.53	0.85	0.68
SJ.4	7.76	22.25	1.76	2.59	1.36	12.53	0.04	618.39	536.22	82.17	86.80	0.81	0.69
SJ.6	5.53	15.84	1.98	2.00	1.47	9.95	0.07	464.28	386.16	78.12	81.77	0.84	0.74
SJ.8	4.88	17.34	2.30	1.82	1.56	11.50	0.06	519.44	440.00	79.45	92.66	0.86	0.72
SJ.10	5.50	19.26	2.42	1.90	1.65	13.12	0.06	513.77	435.33	78.44	85.10	0.89	0.64
SJ.12	3.37	6.37	1.66	1.75	1.16	4.36	0.17	477.20	327.99	149.21	124.12	0.87	0.69
SJ.14	6.05	17.63	<	2.11	1.47	10.75	0.06	279.38	240.13	39.25	42.86	0.83	0.74
SJ.16	5.12	14.20	1.69	1.84	1.59	9.51	0.07	475.05	400.43	74.62	79.04	0.87	0.68
SJ.19	4.91	29.38	3.83	1.88	1.81	18.50	0.03	1271.63	1112.32	159.31	225.91	0.82	0.70
SJ.22	6.09	18.73	1.87	2.00	1.57	11.97	0.05	423.34	364.33	59.00	63.53	0.85	0.65
Estonia OS	3.85	7.31	1.53	1.67	1.46	4.67	0.12	84.60	64.04	20.56	18.69	0.80	0.67
Utah OS	4.24	12.37	2.10	1.81	1.40	8.30	0.08	183.53	146.48	37.05	36.64	0.86	0.59
Jordan OS	4.08	5.80	1.18	1.90	1.09	2.83	0.21	145.44	97.87	47.57	34.76	0.64	0.81
Upper crust	La/Sm	La/Yb	Gd/Yb	La/Pr	Gd/Dy	Ce/Yb	Lu/La	ΣREE(ppm)	LREE(ppm)	HREE(ppm)	MREE(ppm)	Eu/Eu*	Ce/Ce*
C.5	1.62	2.76	1.36	1.32	1.39	2.29	0.37	19.91	12.04	7.87	7.44	0.95	1.09
C.8	1.38	1.81	1.35	1.25	1.22	1.52	0.49	18.57	9.47	9.10	7.84	0.93	1.11
C.10	1.63	2.46	1.43	1.39	1.29	1.89	0.43	22.18	12.33	9.85	8.91	0.89	1.12
C.12	1.70	2.69	1.57	1.39	1.25	2.15	0.34	22.61	12.76	9.85	9.00	0.93	1.07
C.19	1.78	3.34	1.70	1.42	1.42	2.61	0.35	22.03	13.21	8.81	8.44	0.92	1.09
C.22	1.94	2.76	1.37	1.49	1.23	2.05	0.39	18.14	10.34	7.80	6.79	0.89	1.04
C.28	2.28	4.44	1.72	1.63	1.33	2.92	0.24	32.91	20.90	12.02	11.75	0.81	1.00
C.29	2.04	2.65	1.40	1.50	1.12	2.42	0.37	130.19	72.98	57.21	48.29	1.09	0.98
C.32	2.31	3.28	1.44	1.65	1.23	2.05	0.32	13.77	7.89	5.88	5.03	0.78	1.02
C.33b	2.42	3.06	1.13	1.76	1.07	1.71	0.30	19.41	10.91	8.49	6.92	0.71	0.92
YC.2	2.16	8.03	2.80	1.52	1.74	6.53	0.10	29.04	21.37	7.67	9.70	0.98	0.95
YC.5	1.97	2.49	1.30	1.58	1.11	1.75	0.40	19.52	10.52	8.99	7.55	0.86	1.05
YC.6	1.58	2.84	1.69	1.34	1.28	2.36	0.35	23.98	13.93	10.05	9.72	0.95	1.08
YC.7	1.66	2.99	1.55	1.41	1.38	2.32	0.36	19.00	11.34	7.66	7.28	0.91	1.02
YC.10	1.28	1.62	1.28	1.29	1.13	1.37	0.65	21.15	10.27	10.87	9.00	0.95	1.04
YC.12	1.46	2.46	1.62	1.36	1.17	1.99	0.45	18.91	10.32	8.60	7.90	0.94	1.09
YC.13	1.56	2.26	1.48	1.34	1.19	1.77	0.50	22.27	11.84	10.43	9.22	0.89	1.15
YC.14	1.37	1.92	1.40	1.30	1.18	1.63	0.55	20.25	10.40	9.85	8.54	0.96	1.04
YC.15	1.37	1.65	1.39	1.26	1.23	1.37	0.68	21.87	10.47	11.40	9.40	0.93	1.17
SJ.2	1.23	1.87	1.36	1.25	1.27	1.49	0.53	15.04	7.90	7.14	6.39	0.88	1.08
SJ.4	1.94	2.47	1.23	1.68	1.04	1.72	0.38	19.27	10.31	8.95	7.58	0.87	1.09
SJ.6	1.38	1.76	1.39	1.30	1.12	1.37	0.66	16.58	8.07	8.51	7.21	0.88	1.15
SJ.8	1.22	1.92	1.61	1.18	1.19	1.58	0.53	18.01	9.36	8.65	8.00	0.89	1.14
SJ.10	1.37	2.14	1.70	1.24	1.26	1.80	0.57	17.48	8.90	8.58	7.47	0.93	1.00
SJ.12	0.84	0.71	1.17	1.14	0.88	0.60	1.60	23.94	7.73	16.21	11.56	0.90	1.05
SJ.14	1.51	1.96	1.15	1.37	1.12	1.48	0.56	9.12	4.87	4.25	3.64	0.87	1.17
SJ.16	1.28	1.58	1.19	1.19	1.22	1.30	0.65	16.47	8.33	8.14	6.83	0.90	1.07
SJ.19	1.23	3.26	2.68	1.22	1.38	2.54	0.31	41.05	23.60	17.45	19.29	0.86	1.09
SJ.22	1.52	2.08	1.31	1.30	1.20	1.64	0.51	13.67	7.27	6.40	5.44	0.89	1.02
Estonia OS	0.96	0.81	1.07	1.09	1.11	0.64	1.16	3.72	1.45	2.27	1.72	0.82	1.03
Utah OS	1.06	1.37	1.47	1.17	1.07	1.14	0.81	7.16	3.15	4.01	3.22	0.90	0.91
Jordan OS	1.02	0.64	0.83	1.23	0.83	0.39	2.00	7.46	2.31	5.15	3.23	0.67	1.23
NASC	La/Sm	La/Yb	Gd/Yb	La/Pr	Gd/Dy	Ce/Yb	Lu/La	ΣREE(ppm)	LREE(ppm)	HREE(ppm)	MREE(ppm)	Eu/Eu*	Ce/Ce*
C.5	2.07	3.76	1.33	1.64	1.52	3.10	0.27	15.60	10.25	5.35	5.22	1.02	1.06
C.8	1.77	2.47	1.32	1.55	1.34	2.05	0.35	14.15	7.98	6.18	5.47	1.01	1.08
C.10	2.09	3.36	1.39	1.72	1.41	2.55	0.31	17.17	10.46	6.71	6.23	0.96	1.09
C.12	2.18	3.67	1.53	1.72	1.37	2.90	0.25	17.55	10.86	6.70	6.29	1.00	1.05
C.19	2.28	4.56	1.66	1.76	1.55	3.53	0.26	17.27	11.27	6.00	5.91	0.99	1.06
C.22	2.49	3.76	1.33	1.84	1.34	2.77	0.28	14.15	8.85	5.31	4.74	0.96	1.01

Continued Table 9

NASC	La/Sm	La/Yb	Gd/Yb	La/Pr	Gd/Dy	Ce/Yb	Lu/La	ΣREE(ppm)	LREE(ppm)	HREE(ppm)	MREE(ppm)	Eu/Eu*	Ce/Ce*
C.28	2.92	6.05	1.68	2.01	1.45	3.94	0.17	26.18	17.99	8.19	8.24	0.87	0.98
C.29	2.62	3.62	1.37	1.85	1.23	3.27	0.27	101.68	62.84	38.84	33.59	1.17	0.96
C.32	2.96	4.47	1.41	2.04	1.34	2.76	0.23	10.77	6.78	4.00	3.51	0.83	0.99
C.33b	3.10	4.18	1.10	2.18	1.17	2.30	0.22	15.17	9.42	5.76	4.82	0.76	0.90
YC.2	2.77	10.95	2.73	1.88	1.90	8.81	0.07	23.70	18.47	5.23	6.85	1.05	0.92
YC.5	2.52	3.40	1.27	1.95	1.21	2.36	0.29	15.09	8.99	6.10	5.25	0.92	1.02
YC.6	2.02	3.87	1.65	1.66	1.40	3.19	0.25	18.66	11.83	6.84	6.80	1.03	1.05
YC.7	2.13	4.08	1.52	1.75	1.51	3.14	0.26	14.88	9.66	5.22	5.11	0.98	0.99
YC.10	1.64	2.21	1.25	1.60	1.24	1.85	0.47	16.03	8.64	7.38	6.26	1.03	1.02
YC.12	1.87	3.35	1.58	1.69	1.28	2.69	0.33	14.56	8.72	5.83	5.51	1.01	1.07
YC.13	2.00	3.09	1.45	1.66	1.30	2.38	0.36	17.09	10.01	7.08	6.43	0.96	1.12
YC.14	1.76	2.62	1.36	1.60	1.29	2.20	0.40	15.47	8.78	6.68	5.94	1.03	1.02
YC.15	1.75	2.24	1.36	1.56	1.35	1.85	0.49	16.53	8.79	7.75	6.54	1.00	1.14
SJ.2	1.57	2.55	1.33	1.55	1.39	2.00	0.39	11.49	6.63	4.86	4.47	0.95	1.05
SJ.4	2.48	3.37	1.20	2.08	1.13	2.32	0.28	14.89	8.81	6.08	5.27	0.93	1.06
SJ.6	1.77	2.40	1.35	1.61	1.23	1.84	0.48	12.55	6.77	5.78	5.01	0.95	1.13
SJ.8	1.56	2.62	1.57	1.46	1.30	2.13	0.38	13.71	7.83	5.88	5.59	0.96	1.11
SJ.10	1.76	2.91	1.66	1.53	1.38	2.43	0.42	13.34	7.51	5.83	5.20	1.01	0.98
SJ.12	1.08	0.96	1.14	1.41	0.97	0.81	1.16	17.31	6.34	10.97	7.96	0.98	1.03
SJ.14	1.93	2.67	1.13	1.70	1.23	1.99	0.40	7.00	4.12	2.88	2.54	0.94	1.14
SJ.16	1.64	2.15	1.16	1.48	1.33	1.76	0.47	12.54	7.00	5.54	4.77	0.98	1.05
SJ.19	1.57	4.45	2.62	1.51	1.51	3.43	0.22	31.65	19.75	11.90	13.51	0.93	1.07
SJ.22	1.95	2.83	1.28	1.61	1.31	2.22	0.37	10.51	6.16	4.35	3.79	0.97	1.00
Estonia OS	1.23	1.11	1.05	1.34	1.22	0.86	0.84	2.75	1.20	1.55	1.20	0.90	1.01
Utah OS	1.35	1.87	1.43	1.45	1.17	1.54	0.59	5.35	2.63	2.72	2.24	0.97	0.89
Jordan OS	1.30	0.88	0.81	1.53	0.91	0.52	1.45	5.37	1.89	3.48	2.22	0.72	1.21

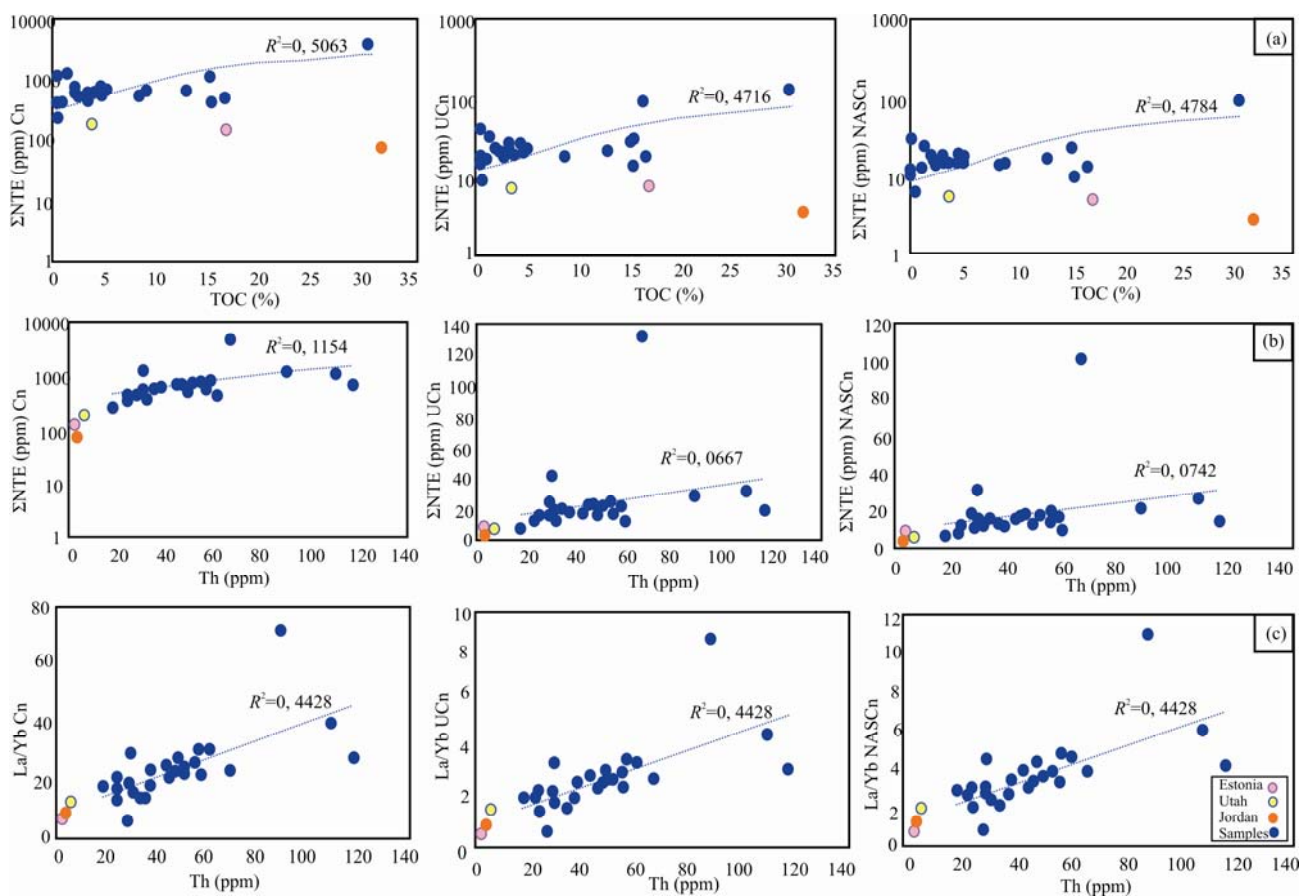


Fig. 12. (a) ΣREE and TOC linear correlation; (b) diagram showing very weak positive correlation between ΣREE and Th; (c) diagram showing a weak positive correlation between La/Yb and Th normalized to Chondrite (C_n), normalized to Upper Crust (UC_n) and normalized to North American Shale Composite ($NASC_n$) of oil shale samples from Estonia-Utah-Jordan and the Celtek Formation in Sorgun Basin.

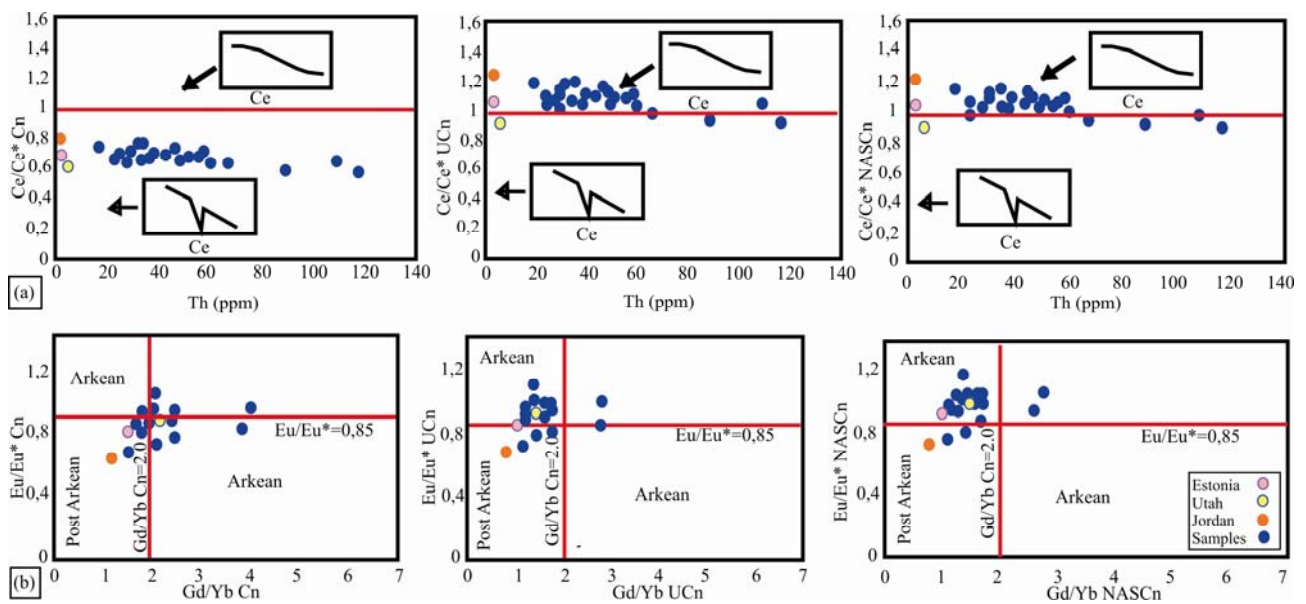


Fig. 13. (a) Th anomalies vs. Ce/Ce^* (after Dia et al., 2000); (b) Gd/Yb diagram vs. Eu/Eu^* normalized to chondrite (C_n), normalized to upper crust (UC_n) and normalized to North American Shale Composite ($NASC_n$) of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after McLennan and Taylor, 1991).

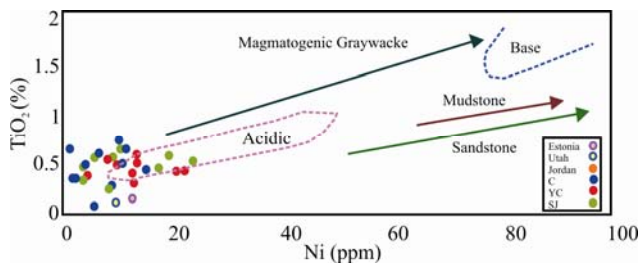


Fig. 14. Diagram of Ni vs. TiO_2 of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after Floyd et al., 1989) (samples are usually close to acidic source).

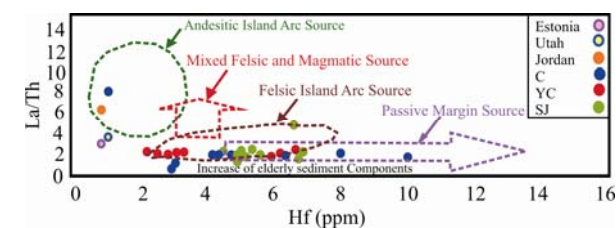


Fig. 15. Diagram of La/Th vs. Hf of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after Floyd and Leveridge 1987).

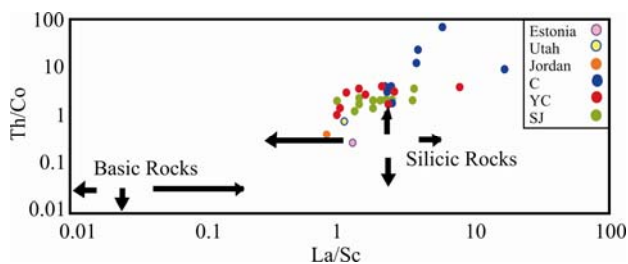


Fig. 16. Diagram of La/Sc vs. Th/Co of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after Cullers, 2002).

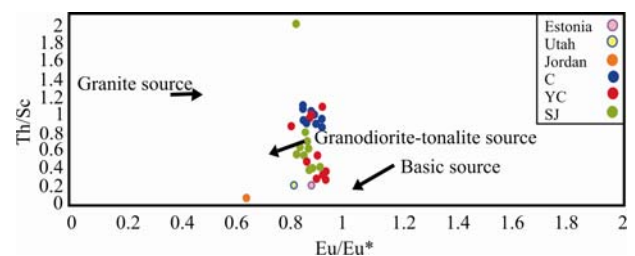


Fig. 17. Eu/Eu^* vs. Th/Sc diagrams of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after Cullers and Podkovyrov, 2002).

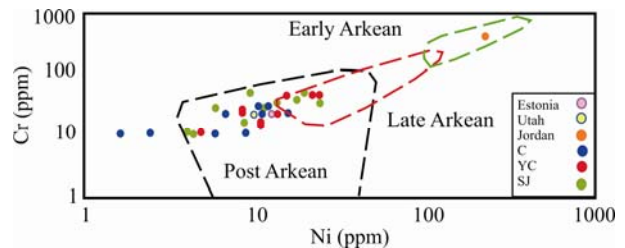


Fig. 18. Ni vs. Cr diagram of oil shale samples from Estonia-Utah-Jordan and the Çeltekk Formation in Sorgun Basin (after Dia et al., 2000).

Since lanthanide group elements show very small differences in their geochemical behavior, their assessment is particularly important for understanding the evolution of the hydrosphere and lithosphere.

Normalized REE patterns of studied samples generally follow the order of LREE>MREE>HREE and are represented by negative Ce and positive Eu anomalies.

REE patterns in organic materials are distinguished as normal (N), light (L), middle (M) and heavy (H), which may display variations in the formation of organic material in different microenvironments.

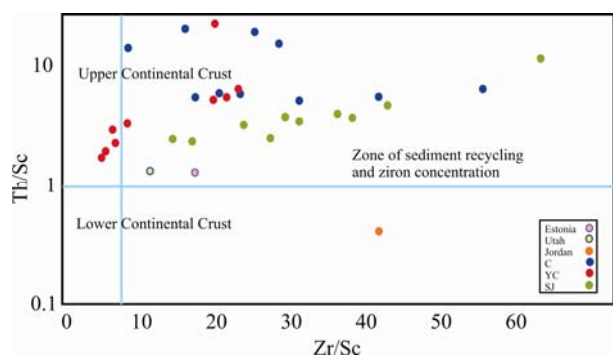


Fig. 19. Plot of Th/Sc vs. Zr/Sc of oil shale samples from Estonia-Utah-Jordan and the Celtek Formation in Sorgun Basin (after McLennan et al., 1993).

For example, MREE enrichment may be recognized in high-salinity and acidic fresh water lakes (Johannesson et al., 1996; Johannesson and Zhou, 1999) and also in a variety of terrestrial waters including rivers (Hannigan and Sholkovitz, 2001). MREE enrichments are not an indicator for high-pH systems (modern seawater; Johannesson et al., 1996) or alkaline lakes (Möller and Bau, 1993) and they mostly represent low-pH waters.

MREE enrichments are affected by some processes such as colloids (Elderfield et al., 1990) and grain/mineral-fluid interaction (Sholkovitz, 1995) and MREE enrichment is initiated via dissolution of mineral surfaces in the aquifer material by acidic waters and surface complexes (Johannesson and Zhou, 1999).

The nature of REE accumulation, which has an economic importance in organic rocks, is closely related to organic material type and the physicochemical conditions of the depositional environment (Jones and Manning, 1994). Due to their organic affinity, HREEs are enriched much more than LREEs and a MREE-rich environment occurs in humic material-rich samples. Regarding paleoenvironment and geological conditions, in most oil shales and some coals HREE is much more enriched than LREE and there may also be LREE and MREE enrichments as well.

A positive Eu anomaly in sediments generally indicates that the effects of CO₂ content and diagenesis are not significant. REEs may be mobilized during organic matter formation under low temperatures and strong reducing conditions.

Eu-enrichment is attributable to alteration of plagioclases in sediments (McLennan et al., 1993). Under anoxic conditions, the diagenetic mobilization of Eu and its reconcentration may also result in positive Eu anomaly (MacRae et al., 1992). Hydrothermal fluids at a mid-ocean ridge are the reason for a positive Eu anomaly in the seawater (Danielson et al., 1992; Pirajno and Van Kranendonk, 2005). Unlike offshore fluids, hydrothermal fluids display significant Eu and LREE enrichment. In general, LREE enrichment patterns and positive Eu anomalies correspond to the physicochemical conditions in hydrothermal systems (Leleyter et al., 1999). In these areas, hot and acidic waters interact with basaltic rocks and then mix with cold seawater of a basic character. In some recent works, REE fraction patterns in river and soil

waters are found to vary due to surficial alteration of apatites, which may result in MREE enrichment and a negative Ce anomaly in river sediments. Organic material content in sediments is suggested to exert a great control over the formation of such patterns (Holland, 1984; Tricca et al., 1999). In other words, if the positive Eu anomaly which is related to MREEs (relatively enriched in modern river waters) has an oxidation state of +2, Eu may be liberated as a result of surficial alteration processes. Feldspar-bearing source rocks liberate Eu²⁺ by a chemical change as a result of the decomposition of organic matter and the increase in the CO₂ level of the Archean atmosphere (Nesbitt, 1979). Therefore, in areas of surficial alteration, the pH of fluids is decreased (Bordenave, 1993). Organic matter of various types may accumulate different elements in varying amounts (Van Buchem et al., 2005).

6 Conclusions

The presence of REE in organic materials can be attributed to various sources. In some cases, REEs as part of the primary composition are found in acid-resistant pyrite, zircon and rutile minerals as metal-organic complexes and in minerals that are protected from acids by the organic material and REEs that are incorporated to the organic material afterwards, and, transported from granitic rocks to the fluids, may also be precipitated or adsorbed in the medium.

Inorganic element ratios and tectonic provenance properties indicate that the organic material components of oil shales of the lower Eocene Celtek Formation were deposited in micro-environments in a transition zone (from land to the sea) under physico-chemical conditions changing from oxic to euxinic in character. According to environmental and source rock assessments, based on element enrichments and element ratios, the source rock was probably a sedimentary rock which was formed by the weathering of a felsic or acidic type magmatic rock, such as granite.

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About the first author



YAVUZ PEHLİVANLI Berna, born in 1980 in Kozan City of Adana Province in Turkey. Her undergraduate work was completed at the University of Nigde Omer Halisdemir in 2001 and her graduate work was at the same institution in 2006. She received her Ph. D. in ore deposits and geochemistry from the University of Ankara (Turkey) in 2011. Her primary specialization is ore deposit, economic geology, element geochemistry, rare earth element geochemistry, radioactive element geochemistry, stable isotopes geochemistry fluid inclusion, ore microscopy, organic geochemistry, oil shale. She has worked as an assistant professor at the University of Yozgat Bozok (Turkey) since 2011. E-mail: bernayavuz80@gmail.com.