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Organic Geochemical and Mineralogical Effect on Element Enrichment of Cayirhan Oil Shales, Beypazari, Ankara, Turkey

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Abstract

The concentrations of minerals and trace elements in the Çayırhan oil shale (ÇOS) (Beypazari, Ankara / Turkey) were determined by XRD and ICP-MS. Total organic carbon (TOC) content of ÇOS was examined to have higher values (TOC 2.08%-23.29%, average 9.53%). The account of average shale enrichment factors of ÇOS is determined to enrich the elements such as Mn, Mg, Pb, Si, Sr, Zr, K, Ca, Na, U, Ba, Cu, Ni, As, V, Co, Mo, Rb Fe, P, Ti, Sb and Cd, however, to consume the elements such as Cr and Zn. Element enrichment in sediments is generally presumed to come from different sources. Mineral content in oil shale is also effective for enrichment of elements. When the amount of organic matter in rocks increases, it can lead to the enrichment of elements such as U, W, Hf, Ce, Ba, I, Sb, Cd, Mo, Rb, Se, As, Ge, Zn, Cu, Ni, Co, Cr and V. Element content of oil shale can affected by either organic compounds or inorganic compounds. Minerals such as Albite, Alabandite, Ankerite, Analcime, Barite, Dolomite, Glauconite, Gypsum, Calcite, Clay Minerals, Clinoptilolite, Quartz, Kutnohorit, Magnesite, Marcasite, Microcline, Muscovite, Natrolite, Orthoclase, Pyrite, Pyrochlore, Raspit, Sanidine, Saponite, Sphalerite, Spinel, Talc, Titanomagnetite, Vermiculite and Zeolite were observed in the samples of ÇOS. It is thought that the chemical composition of these minerals also contributes to the enrichment of elements.

Keywords: Mineral content, oil shales, ICP-MS, XRD, Total organic carbon (TOC), Çayırhan oil shale (ÇOS), (Beypazari, Ankara, Turkey)

Çayirhan Petrollü Şeyllerinin Element Zenginleşmelerine Organik Jeokimyasal ve Mineralojik Etki, Beypazari, Ankara, Turkey

Özet

Çayırhan petrol şeylleri (ÇOS) (Beypazarı, Ankara / Türkiye) içerisindeki mineral ve eser element konsantrasyonları XRD ve ICP-MS ile belirlenmiştir. ÇOS'un toplam organik karbon (TOC) içeriğinin oldukça yüksek değerlere (TOC 2.08 % -23.29, ortalama % 9.53) sahip olduğu belirlenmiştir. ÇOS'un ortalama şeyle göre zenginleşme faktörleri hesaplandığında, Mn, Mg, Pb, Si, Sr, Zr, K, Ca, Na, U, Ba, Cu, Ni, As, V, Co, Mo , Rb Fe, P, Ti, Sb ve Cd gibi elementlerin zenginleştiği ancak Cr ve Zn gibi elementlerin ise tüketildiği belirlenmiştir. Sedimanlar içindeki element zenginleştirmesinin genellikle farklı kaynaklardan geldiği düşünülmektedir. Kayaçlardaki organik madde miktarı arttıkça U, W, Hf, Ce, Ba, I, Sb, Cd, Mo, Rb, Se, As, Ge, Zn, Cu, Ni, Co, Cr ve V gibi elementlerin zenginleşmesine neden olabilir. Petrol şeyllerinin element içeriği ya organik bileşiklerden ya da inorganik bileşiklerden etkilenir. ÇOS örnekleri içinde Albit, Alabandit, Ankerit, Asalit, Barit, Dolomit, Glokonit, Alçı, Kalsit, Kil Mineralleri, Klinoptilolit, Kuvars , Kutnohorit, Magnesit, Markasit, Mikroklin, Muskovit, Natrolit, Orthoklas, Pirit, Piroklore, Raspit, Sanidin, Saponit, Sfalerit, Spinel, Talk, Titanomanyetit, Vermikülit ve Zeolit gibi mineraller gözlenmiştir. Bu minerallerin kimyasal bileşiminin de elementlerin zenginleşmesine katkıda sağladığı düşünülmektedir.

Anahtar Kelimeler: Mineral içeriği, petrol şeylleri, ICP-MS, XRD, Toplam organik karbon (TOC), Çayırhan petrol şeylleri (ÇOS) (Beypazarı, Ankara / Türkiye).

1. Introduction

The middle Miocene Epoch, organic-rich oil shales, which are exposed in the area between Beypazarı and Nallıhan towns in city of Ankara, have been investigated by means of differentiation of organic-matter bearing geological units, tectonic basin, organic matter component of rocks and their economical potential (Aziz, 1976; Akkuş et al., 1982; Şener and Sengüler, 1991; Özçelik, 2002; Gülbay and Korkmaz, 2005; Sarı and Aliyev, 2006, Yavuz Pehlivanlı 2011, Yavuz Pehlivanlı et al. 2013a,b).

It is estimated that the investigation site hosts a potential reservoir of 300 million tons of oil shales with calorific value of more than 1000 k cal/kg and another 900 million tons with calorific value between 100-1000 k cal/kg (Aziz, 1976). In this respect, examination of oil shales in the area is higly important. In this survey, ÇOSs are systematically analyzed by means of geochemical paleoredox variations depending upon the depth of all samples. Oil shales is one of the most important industrial raw materials for the future.

Oil shales from different localitions have wide compositional variation. Classification of oil shales is based on a number of criteria, including organic composition, mineralogy, specific gravity, and age (Jaffe 1962). Geological classification can be made based on the environment of shale deposits (i.e., deltaic, swamp, estuarine or coastalmarine basin). However there is still insufficient data on field relationships, mineralogy, and sedimentary petrology for many oil-shale deposits (Shanks et al. 1976). The results provide a definitive chemical and mineralogical characterization of the oil shale and identify the major mineralogical residences of the important trace elements.

2. Geological Setting and Stratigraphy

Paleocene Kızılbayır formation is the oldest unit in the investigation site. It is unconformably overlain by middle Miocene sedimentary units which consist of, from bottom to the top, Boyalı, Hırka, Karadoruk and Sarıağıl formations. These units are cut by Teke volcanites. Pliocene Softa formation and alluvium cover all these units (Fig. 1). The Çayırhan oil shales that is under investigation are formed within Hırka formation which conformably overlies Boyalı formation with lateral and vertical transitions. Typical section of formation lies around Hırka village where laminated sandstone, claystone, oil shale, carbonaceous shale, dolomitic limestone, tuff, trona and local intraformational breccia occur. Oil shales of Hırka formation varying between gray to light-dark brown colours are very thin bedded. Oil shales with 8-22 m thickness are layered with dolomitic limestone and tuffs (Yavuz Pehlivanlı 2011).

3. Samples and Analytical Methods

In this research, a total of 205 samples were examined which were collected from out crops (B and C measured stratigraphic sections MSS), gallery (CG gallery) and boreholes (S, PM and PR boreholes) (Table 1). Samples were taken from measured stratigraphic sections, core boxes of boreholes drilled in the area and in coal galleries from levels cutting the oil shales of Hırka formation (Yavuz Pehlivanlı 2011).

Inorganic geochemical analysis of samples was carried out at ACME Laboratories in Canada. XRD, SEM-EDX and TOC-Pyrolysis analysis was conducted at Turkish Petroleum Corporation (TPAO) Laboratories. Standard XRD whole-rock analysis was conducted in 2-60 2 Theta (ϴ) range and at 1-2°/min. scan speed. Standard XRD clay pattern analysis consists of regular analysis conducted in 2-30 2 (ϴ) range and at 1°/min. scan speed, ethylene glycolated scan in 2-20 2 ϴ range and heated scan in 2-15 2 ϴ range. “Overnight” XRD whole-rock analysis was carried out for 8 hours in 2-60 2 ϴ range and at a scan speed of 0,125 °/min (Table 1).

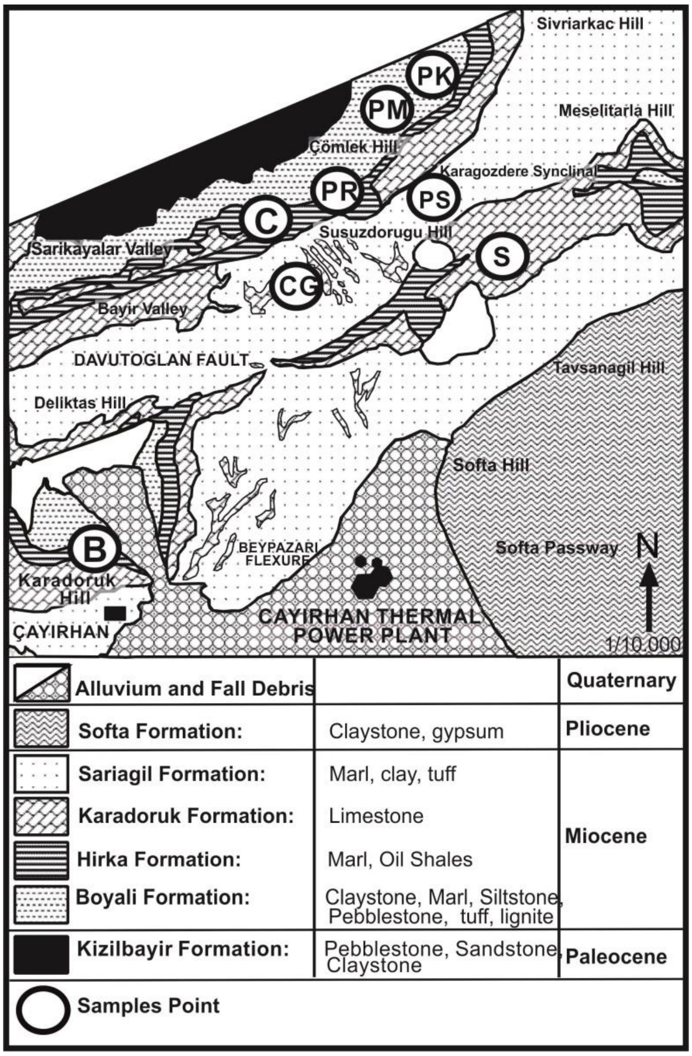

Fig. 1. Geological map of the study area (Inci et al. 1988).

Table 1. Analysis of samples evaluated in this study (Yavuz Pehlivanlı, 2011).

Sample Points	XRD	SEM-EDX	ICP-MS	TOC - PYROLYSIS
B	9	3	56	7
C	11	3	34	10
CG	8	2	21	5
PK	11	2	11	6
PM	11	-	11	10
PR	11	-	11	11
PS	11	4	10	8
S	28	11	49	4
Total	100	25	205	61
Analyzing the instrumentalities	**By Rigaku D/Max 2200 Ultima/PC in TPAO(Turkive)**	**By (EDS / IXRF) (JEOL - JMS 6490 LV) in TPAO (Turkive)**	**By ICP-MS in ACME (Canada)**	**By Rock-Eval VI in TPAO (Turkive)**

4. Results and Discussion

Oil shales formed in different environments have different chemical and mineralogical contents. The classification of oil shale is usually made according to differences in the amount and type of organic matter, mineralogical content, content of inorganic matter, formation conditions and age of formation (Shanks et al 1976). Himus (1951) suggested that the inorganic content in oil shales devided into detrital mineral (generally quartz, felsispars, clay minerals and volcanic debris), biogenic mineral (pirimarily amorphous silica and calsium carbonate) and autogenic mineral (pyrite, and others metal sulphides, calsite, dolomite, siderite, chert, phosphates, and saline minerals such as trona). Authigenic minerals provide important information redox conditions during or soon after sedimentation, natural of the original solution and climatic conditions. Organic matter and authigenic minerals are usually formed in reducing environments (low Eh) (Shanks et al 1976). So that the mineralogical content of the incoming material directly affects the enrichment of the element.

4.1. Mineralogical Investigations

The element content of the oil shale influences both inorganic compounds and organic compounds. The samples taken from the investigation area have consistence of minerals such as Albite, Alabandite, Ankerite, Analcime, Barite, Dolomite, Glauconite, Gypsum, Calcite, Clay Minerals, Clinoptilolite, Quartz, Kutnohorit, Magnesite, Marcasite, Microcline, Muscovite, Natrolite, Orthoclase, Pyrite, Pyrochlore, Raspite, Sanidine, Saponite, Sphalerite, Spinel, Talc, Titanomagnetite, Vermiculite and Zeolite which are identified by XRD techniques (Table 2). These minerals are also characterized by thin sections, polished sections and SEM-EDAX techniques (Fig 2-4). When the mineral content of the samples is considered, we can say that the element enrichment is affected by mineral content (Tablo 2).

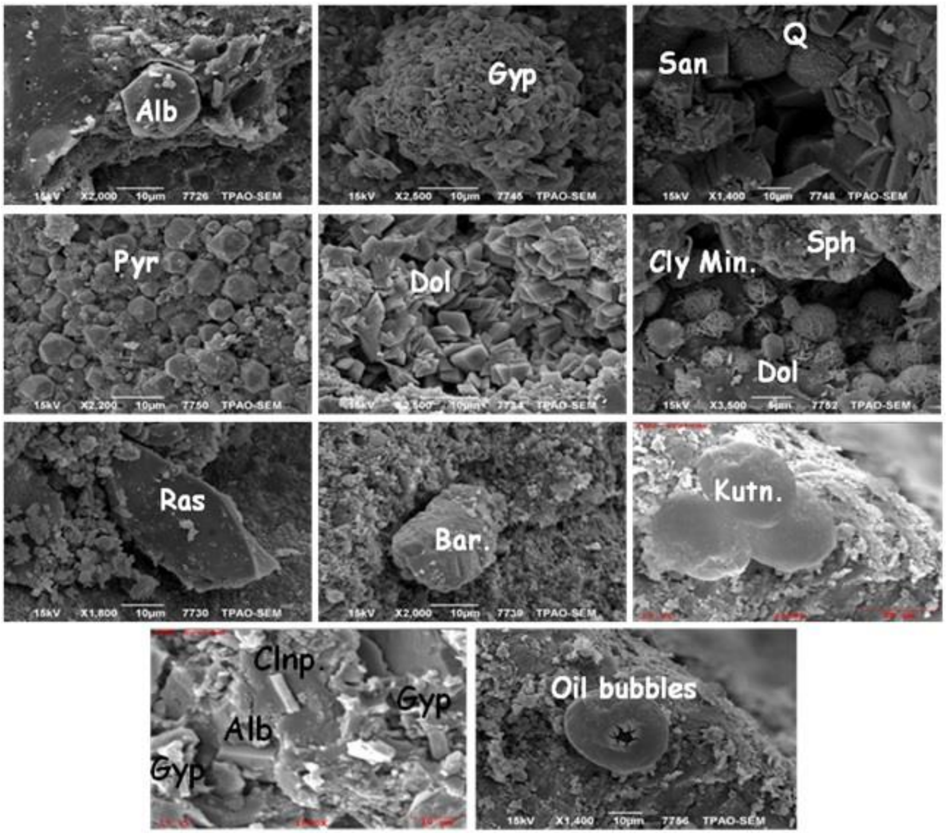

Fig.2. Photomicrographs of some of the minerals identified by SEM-EDX (Alb: Albite, Gyp: Gypsum, San: Sanidine, Q: Quartz, Pyr: Pyrite, Dol: Dolomite, Cly Min: Clay Minerals, Sph: Sphalerite, Ras: Raspit, Bar: Barite, Kutn: Kutnohorite, Clnp: Clinoptilolite).

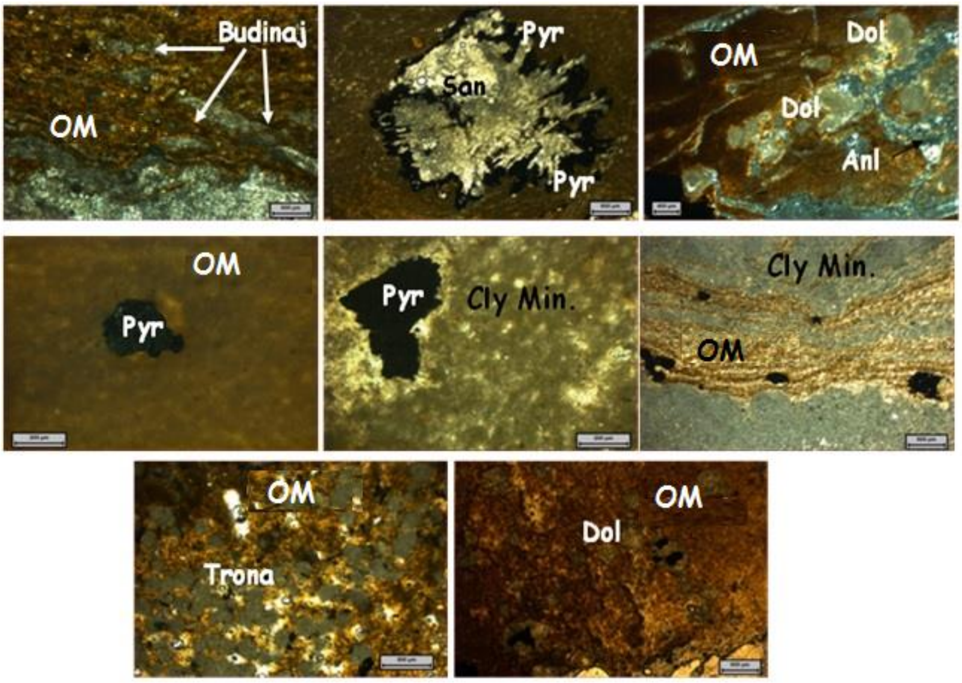

Fig.3. Photomicrographs of some of the minerals identified by thin section (San: Sanidine, Pyr: Pyrite, Dol: Dolomite, Anl: Analcime Cly, Min: Clay Minerals, OM: Organic Matter).

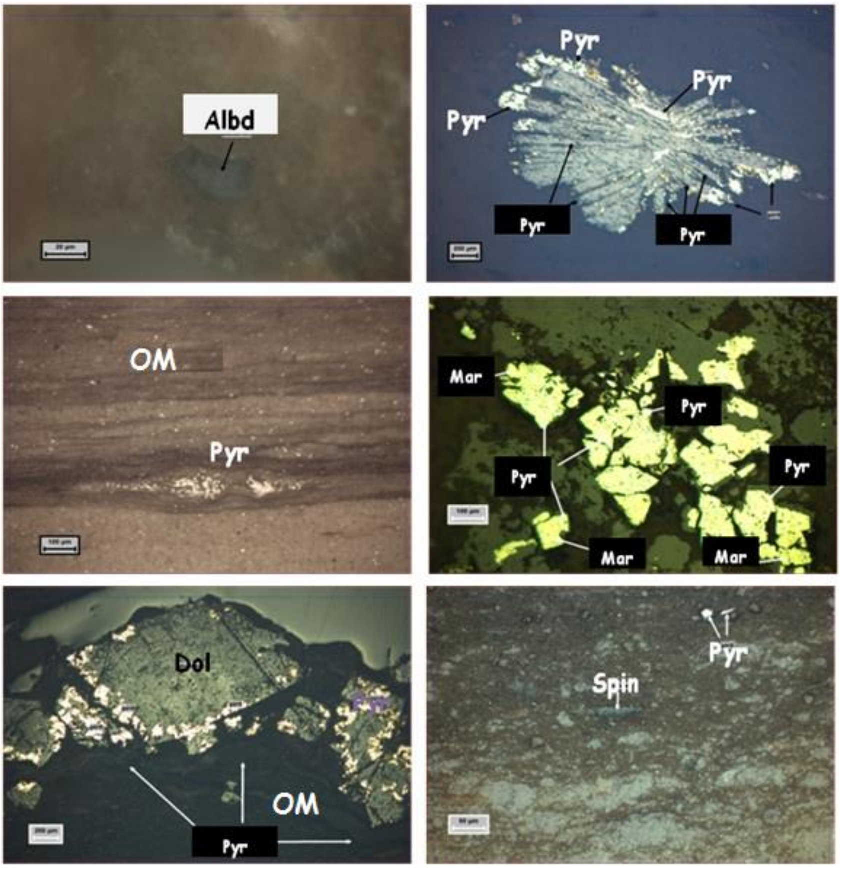

Fig.4. Photomicrographs of some of the minerals identified by ore microscopy (Albd: Alabandite Pyr: Pyrite, Mar: Marcasite, Dol: Dolomite, Spin: Spinel, OM: Organic Matter).

Table 2. Minerals determined and formulas by XRD analysis in the ÇOS samples.

SUMMARY	MINERAL NAME	MINERAL FORMULA
Alb	Albite	Na Al Si_3 O_8
Albd.	Alabandite	MnS
Ank.	Ankerite	Ca(Fe++,Mg,Mn)(CO3)2
Anl.	Analcime	NaAlSi2O6•(H2O)
Bar.	Barite	BaSO4
Dol	Dolomite	CaMg(CO3)2
Gul.	Glauconite	(K,Na)(Fe+++,Al,Mg)2(Si,Al)4O10(OH)2
Gyp.	Gypsum	CaSO4•2(H2O)
Cal.	Calcite	CaCO3
Cly Min.	Clay Minerals	(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2•n(H2O)
Clnp.	Clinoptilolite	(Na,K,Ca)2-3Al3(Al,Si)2Si13O36•12(H2O)
Q	Quartz	SiO2
Kutn.	Kutnohorite	Ca(Mn,Mg,Fe++)(CO3)2
Mag.	Magnesite	MgCO3
Mar.	Marcasite	FeS2
Mic.	Microcline	KAlSi3O8
Mus.	Muscovite	$(Kal_2(Al_2\ Si_3\ O_{10})\ (OH)_2$,
Natr.	Natrolite	$Na0.3Fe^{+++}2(Si,Al)4O10(OH)2•n(H2O)$
Ort.	Orthoclase	$K[AlSi_3O_8]$
Pyr	Pyrite	FeS2
Pyroc.	Pyrochlore	$(Ca,Na)_2Nb_2O_6(O,OH,F)$
Ras	Raspit	PbWO4
San.	Sanidine	(K,Na)(Si,Al)4O8
Sap.	Saponite	(Ca/2,Na)0,3(Mg,Fe++)3(Si,Al)4O10(OH)2•4(H2O)
Sph.	Sphalerite	ZnS
Spin.	Spinel	MgAl2O4
Tlc.	Talc	Mg3Si4O10(OH)2
TitM	Titanomagnetite	$Fe(Fe_{0.75}Ti_{0.25})_2O_4$
Ver.	Vermiculite	(Mg,Fe++,Al)3(Al,Si)4O10(OH)2•4(H2O)
Zeo.	Zeolite	Mx, Dy (ALx+2y Si n-x+2y O2n). m H2O dir. M= Na,K veya diğer(+1) değerlikli katyonlar, D= Ma, Ca, Si, Ba ve diğer (+2) değerli katyonlardır.

4.2. Organic Geochemical Studies

Amount of Organic Matter

TOC values of Çayırhan oil shales (ÇOS) in Hırka Formation (Middle Miocene) range from 2.08 to 48.48 wt %, average 10,013 wt % (Table 3). According to various researchers, TOC values of ÇOS samples are qualified to be enriched (Tissot and Welte, 1984), very good (Jarvie, 1991) and perfect (Peters and Cassa, 1994) source rock potential.

Table 3. Results of the pyrolysis analysis of ÇOS.

Age	Formation Name	Sample Location	Sample No	Total Organic Carbon (wt %)	S1 (mg HC/g)	S2 (mgHC/g)	S3 (mgCO2/g)	HI (Hydrogen Index)	OI (Oxygen Index)	TMAX (C°)	GENETIC POTENTIAL (S1+S2)	Pİ (PRODUCTION INDEX) (S1/S1+S2)
MIOCENE	HIRKA FORMATION	SURFACE	B55	12,74	4,4	104,3	4,53	819	36	424	108,74	0,04
			B50	11,58	3,94	105,8	3,03	914	26	438	109,8	0,04
			B46	10,55	1,52	87,78	4,17	832	40	437	89,3	0,02
			B44	10,95	2,33	97,7	3,44	892	31	437	100,03	0,02
			B42	9,34	0,63	76,13	3,68	815	39	438	76,76	0,01
			B39	10,31	1,38	78,6	5,04	762	49	438	79,98	0,02
			B37	17,48	1,56	149,81	6,72	857	38	443	151,37	0,01
			B34	14,36	1,09	128,2	5,08	893	35	441	129,35	0,01
			C33	13,2	1,81	120,2	5,02	911	38	443	122,07	0,01
			C30	9,51	2,95	74,32	3,2	781	34	430	77,27	0,04
			C28	6	0,87	47,23	3,47	787	58	442	48,1	0,02
			C25	18,12	1,42	154,7	7,65	854	42	443	156,17	0,01
			C21	5,35	1,24	39,82	1,89	744	35	438	41,06	0,03
			C17	12,73	1,45	104,91	4,88	824	38	440	106,36	0,01
			C15	4,92	1,02	37,42	2,11	761	43	438	38,44	0,03
			C13	9,1	1,82	75,32	3,02	828	33	438	77,14	0,02
			C11	13,96	1,34	114,77	6,24	822	45	441	116,11	0,01
		GALLERY	C4	3,43	0,21	1,56	6,55	45	191	428	1,77	0,03
			CG1	23,29	0,58	29,19	15,52	125	67	420	29,77	0,01
			CG11	21,59	3,33	195,16	6,73	904	31	447	198,49	0,02
			CG13	4,19	0,62	30,08	1,39	718	33	447	30,7	0,02
			CG15	5,32	1,01	43,4	1,7	816	32	437	44,41	0,02
		BOREHOLE	PR4	15,68	0,33	41,53	15,27	265	97	428	41,86	0,01
			PR5	19,5	0,38	48,87	16,57	251	85	428	49,25	0,01
			PR7	2,08	0,4	9,11	1,64	438	79	425	9,51	0,04
			PR11	3,46	0,76	21,25	1,12	614	32	433	22,01	0,03
			PR17	5,29	1,99	44,34	1,35	838	26	437	46,33	0,04
			PR20	8,65	4,02	73,15	1,67	846	19	421	77,17	0,05
			PR22	8,87	3,19	77,81	2,26	877	25	443	81	0,04
			PR23	6,45	2,87	54,12	1,79	839	28	442	56,99	0,05
			PR25	5,73	2,56	40,09	1,69	700	29	432	42,65	0,06
			PR28	5,73	2,61	46,02	1,77	803	31	442	48,63	0,05
			PR31	9,52	6,18	77,85	2,05	818	22	436	84,03	0,08
			PK2	2,86	1,42	7,46	1,79	261	63	424	8,88	0,15
			PK8	5,61	1,2	41,53	1,59	740	28	423	42,73	0,03
			PK10	19	2,43	171,05	3,54	900	19	442	173,48	0,01
			PK12	17,27	3,92	133,8	4,31	775	25	423	137,79	0,03
			PK14	3,47	1	25,77	0,88	743	25	430	26,77	0,04
			PK22	5,1	2,19	39,05	1,22	766	24	438	41,24	0,05
			PS19	10,41	1,75	89,27	2,88	858	28	445	91,02	0,02
			PS1	7,51	1,16	31,6	2,78	421	37	434	32,76	0,03
			PS2	4,02	0,33	4,71	2,74	117	68	437	5,04	0,04
			PS3	8,35	2,44	64,75	2,14	775	26	433	67,19	0,04
			PS7	10,8	3,16	89,56	1,92	829	18	413	92,72	0,03
			PS9	5,68	4,12	39,15	1,58	689	28	433	43,27	0,10
			PS10	4,4	1,93	32,87	0,94	747	21	440	34,8	0,06
			PS12	6,05	6,13	44,41	1,35	734	22	424	50,54	0,13
			PS48	4,62	3,58	29	1,12	628	24	432	32,58	0,12
			PM2	48,48	0,54	80,41	21,48	166	44	421	80,95	0,01
			PM13	16,37	3,64	126,9	4,21	775	26	428	130,57	0,03
			PM17	12,74	5,12	106,8	2,5	839	20	434	111,96	0,05
			PM18	9,64	4,36	85,68	1,7	889	18	421	90,04	0,05
			PM21	7,01	1,8	60,02	1,88	856	27	443	61,82	0,03
			PM24	9,17	6,07	74,13	1,57	808	17	431	80,2	0,08
			PM27	6,43	1,96	48,15	1,7	749	26	436	50,11	0,04
			PM28	11	7,25	92,6	2,38	842	22	439	99,85	0,08
			PM31	4,04	3,32	23,56	1,2	583	30	434	26,88	0,13
			PM34	11,81	7,47	92,84	3,32	786	28	437	100,31	0,08
			S77	12,85	5,2	104,13	3,12	810	24	424	109,33	0,05
			S83	11,17	2,75	94,91	1,75	850	16	421	97,66	0,03
			S14	3,77	4,29	18,29	1,92	485	51	381	22,58	0,21
			S19	6,41	1,76	49,72	2,35	776	37	443	51,48	0,03

Type of Organic Matter

HI-OI (Espitalié et al., 1977) diagrams were also used to establish kerogen type. Using hydrogen index (HI), oxygen index (OI) and maximum temperature (Tmax) values from the pyrolysis analysis, organic matter type (kerogen type) of ÇOS was determined (Table 3).

In the HI-OI graphic, most samples are plotted in the Type-I kerogen field and a limited number of samples are represented by Type-II kerogen (Figure 5).

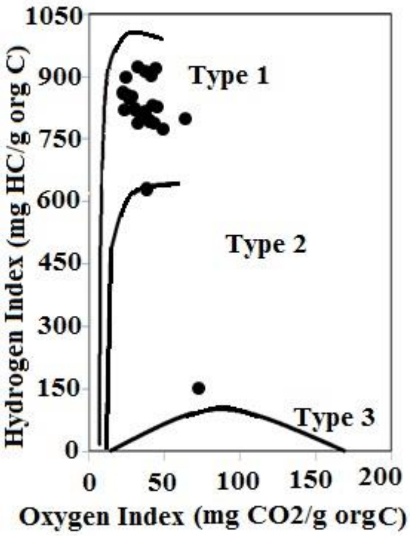

Fig.5. Quantity and characterization of organic matter from outcrop samples in HI-OI diagrams (Espitalie et al., 1977).

Maturity of Organic Matter

T_{max} values of shale samples range between 381 and 447°C (Table 3). Based on T_{max} standards, maturity of investigated samples was categorized within the range of oil window of the most of the samples. Furthermore, in some of the samples, different ranges of distribution values for each level at immature-early mature stage (Espitalié et al., 1985; Peters and Cassa, 1994; Table 3; Figure 6).

Hydrocarbon Generation Potential

To determine hydrocarbon derivation potential of shale samples, HC-TOC (Wehner, 1989) diagram was used.

The Genetic Potential values of examined oil shales are 1770-198490 ppm which yield a good source of rock potential (Tissot and Welte, 1978; Table 3).

The results evaluated in this section are stated in this paragraph . TOC values of ÇOS range from 2.08 to 48.48% (average %10.01) (Yavuz Pehlivanlı, 2011). By using hydrogen index (HI), oxygen index (OI) and maximum temperature (Tmax) values from the pyrolysis analysis, organic matter type (kerogen type) of ÇOS were identified. In the HI-OI graphic, most samples are marked as the Type-I kerogen field and limited number of samples are represented by Type-II kerogen (Fig.5). In addition, kerogen types were also determined by using HI-Tmax graphic (Fig. 6) which indicates similar results.

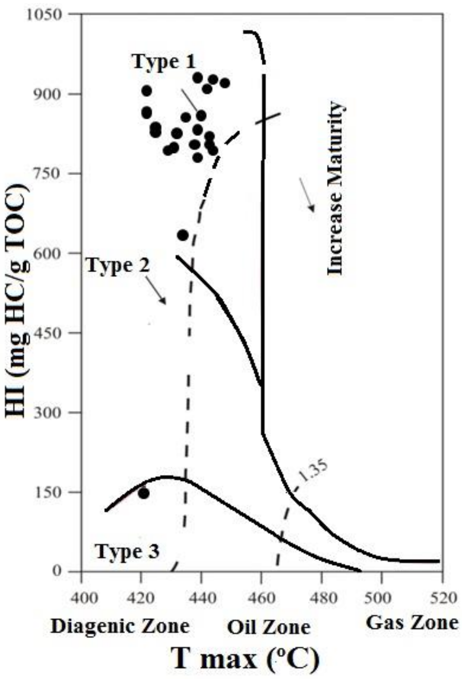

Fig. 6. Plots of Hydrogen Index (HI) vs Tmax ÇOS shale (Mukhopadhyay et al., 1995).

4.3. Element Enrichment

To determine major and trace element enrichments, the concentration of each element was normalised with respect to Al, which is resistant to the alteration, and an enrichment factor (EF) was computed. In calculations, the following formula was used:

$$[EF_{element}\ X = (X/Al)_{sample} / (X/Al)_{average\ sample}]$$ (Brumsack, 2006).

If the EF>1, the element enrichment is available. In contrast, EF<1 elements are depleted.
With respect to WOSAs (the world average shale), all the major elements of the ÇOS and some of the trace elements (Co, Ni, Cu, As, Rb, Sr, Zr, Mo, Cd, Ba, Pb, and U) were found to be enriched to varying extents (Table 4). Mg (16,82 times), Ca (15,30 times), Si (5,80 times), Sr (5,54 times), Mo (5,45 times), As (4,87 times), Cd (4,16 times), K (3,52 times), Co (3,08 times), Sb (2,09 times), V (2,08 times) were the most enriched elements followed by Ni, Mn, Pb, Ba, Rb, Zr, Ti and Cu with enrichments of 1.0- times to 1.9- times (Table 4).
Element enrichment factors are affected by the amount of organic matter and organic matter type. Lithological, mineralogical and chemical composition and physicochemical conditions of the environment are effective in the enrichment of elements in organic-matter rich rocks.

4.4. Possible Sources of Element Enrichments

It is suggested that enrichment of elements in sediments that they came from six different sources. They are to arrive at the elements of the upper and lower sediment diagenesis, to participate of the elements in the environment of suboxic shelf and slope sediments, to effect of hydrothermal activity, the wind, sea waters and to influence of river discharge. The enrichment of elements is usually associated with mineral contents. For example, Al, K, Na, Ti, Rb, Cs, REE, Pb, Tb and Th in feldspar and clay minerals can be enriched as a detrital origin. Elements such as TIC, Ca, Mg, Sr, Ba and Mn can be enriched in the process of dissolution of the calcium lacustrine biogenic origin. TOC and phosphorus is enriched due to the plankton in organic matter.
Further, S and Fe elements are enriched in the appropriate redox conditions in the presence of pyridine; Ni, Cu and Mo elements are enriched to be depend on pyrite and organic material in the redox conditions. Uranium enrichment is dependent on the redox conditions in uraninite or organic matter. In particular, Mg, Ca, Sr and Mn are specific to the carbonate system and are used to describe different carbonate processes. Magnesium (Mg) and strontium (Sr) together with calcium (Ca) always indicate the presence of carbonates (eg dolomite). Mg also occurs in the clay mineral and shows the clay component in the clay in connection with Fe. Some of the magnesium can be found as siderite, ankerite or dolomite. In the mineral structure of calcium carbonate, Sr can take up calcium. Examples of the study area are

summarized element enrichment in Table 4, Possible Sources of enriched elements in rich organic matter rocks in Table 5 (Finkelman, 1993) and the relationship mineral of the rich elements in Table 6.

Table 4. According to the average shale enrichment factors (EF) of All Samples Average (E: Enriched; D: Depleted elements).

Elements	B	C	CG	PK	PM	PR	PS	S	All Samples Average	EF of All Samples Average
Mn	E	E	E	E	E	E	E	E	E	1,54
Mg	E	E	E	E	E	E	E	E	E	16,82
Pb	E	E	E	E	E	E	E	E	E	1,51
Fe	E	E	D	E	E	E	E	D	D	0,83
Si	E	E	E	E	E	E	E	E	E	5,80
Zr	E	E	E	E	E	E	E	D	E	1,24
P	E	E	D	E	D	E	E	D	D	0,32
Sr	E	E	E	E	E	E	E	E	E	5,54
K	E	E	E	E	E	E	E	E	E	3,52
Ti	E	D	D	E	D	E	E	D	E	1,19
Ca	E	E	E	E	E	E	E	E	E	15,30
Na	E	D	E	E	E	E	E	D	D	0,16
Rb	D	D	E	D	E	E	D	E	E	1,25
U	E	E	E	E	E	E	E	E	E	7,44
Ba	E	E	E	E	E	E	E	E	E	1,36
Cu	E	E	E	E	E	E	D	E	E	1,12
Ni	E	E	E	E	E	E	E	E	E	1,84
Cr	D	D	D	D	D	D	D	D	D	0,00
As	E	E	E	E	E	E	E	E	E	4,87
V	E	E	E	E	E	E	E	E	E	2,08
Zn	E	D	D	E	E	D	D	D	D	0,97
Sb	E	D	D	E	D	E	E	D	E	2,09
Co	E	E	E	E	E	E	E	E	E	3,08
Mo	E	E	E	E	E	E	E	E	E	5,45
Cd	E	D	D	E	D	E	D	D	E	4,16

Table 5. Possible Sources of enriched elements in rich organic matter rocks (Finkelman, 1993)

Elements	Origin
Mg	clays
Mn	siderite, calcite
P	phosphates
Ni	sulphides, organic matter, clay.
Pb	galena, pbs
K	-
Fe	pyrite, siderite, sulfates, oxides, organic matter
Si	quartz, clays, silicates
Cu	chalcopyrite
Ti	oxides, clays, organic matter
V	clays, organic matter
Ca	calcite, organic matter, sulfate, potash, silicates
As	solid solution in pyrite (solid solution), organic matter
Cr	clays
Na	organic matter, clays, zeolites, silicates
Zn	sphalerite
Zr	zircon
Rb	may be associated with illite
Sr	carbonates, phosphates, organic matter
Sb	associated with very little sulfide, sometimes organic matter.
U	associated with organic, zircon
Ba	associated with barite, organic matter
Mo	may be associated with sulfide and organics.
Cd	sphalerite,
Co	sulphides, pyridine

Table 6. Relationship mineral of the rich elements summarized in samples of the study area (B-MSS, C-MSS, CG- Gallery, PK-PM-PR-PS and S borehole).

Example	According to average shale		Mineral Contents	
Area	Enriched Elements	Depleted Elements	Mineral Name	Formula
B	Mn, Mg, Pb, Fe, Si, Sr, Zr, P, K, Ti, Ca, Na, U, Ba, Cu, Ni, As, V, Zn, Sb, Co, Mo, Cd	Rb, Cr	clinoptilolite	(Na,K,Ca)2-3Al3(Al,Si)2Si13O36•12(H2O)
			gypsum	CaSO4•2(H2O)
			dolomite	CaMg(CO3)2
			quartz	SiO2
			analcime	NaAlSi2O6•(H2O)
			calcite	CaCO3
			ankerite	Ca(Fe++,Mg,Mn)(CO3)2
			sanidine	(K,Na)(Si,Al)4O8
			magnetism	MgCO3
			orthoclase	KAlSi3O8
			muscovite	KAl2(AlSi3O10),(FOH)2
C	Mn, Mg, Pb, Fe, Si, Sr, Zr, P, K, Ca, U, Ba, Cu, Ni, As, V, Co, Mo,	Ti, Na, Rb,Cr, Zn, Sb, Cd	clinoptilolite	(Na,K,Ca)2-3Al3(Al,Si)2Si13O36•12(H2O)
			quartz	SiO2
			calcite	CaCO3
			muscovite	KAl2(AlSi3O10),(FOH)2
			microkline	KAlSi3O8
			gypsum	CaSO4•2(H2O)
			ankerite	Ca(Fe++,Mg,Mn)(CO3)2
			talc	Mg3Si4O10(OH)2
			sepiolite	Mg4Si6O15(OH)2•6(H2O)
			analcime	NaAlSi2O6•(H2O)
			dolomite	CaMg(CO3)2
			montmorillonite	(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2•n(H2O)
			kaolinite	Al2Si2O5(OH)4
CG	Mn, Mg, Pb, Si, Sr, Zr, K, Ca, Na, U, Ba, Cu, Ni, As, V, Co, Mo, Rb	Fe, P, Ti, Cr, Zn, Sb, Cd	clinoptilolite	(Na,K,Ca)2-3Al3(Al,Si)2Si13O36•12(H2O)
			microkline	KAlSi3O8
			calcite	CaCO3
			talc	Mg3Si4O10(OH)2
			chlorite	Na0,5(Al,Mg)6(Si,Al)8O18(OH)12•5(H2O)
			albite	NaAlSi3O8
			natrolite	Na2[Al2Si3O10]•2(H2O)
			quartz	SiO2
			dolomite	CaMg(CO3)2
			ankerite	Ca(Fe++,Mg,Mn)(CO3)2
			orthoclase	KAlSi3O8
			montmorillonite	(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2•n(H2O)
PK	Mn, Mg, Pb, Fe, Si, Sr, Zr, P, K, Ti, Ca, Na, U, Ba, Cu, Ni, As, V, Zn, Sb, Co, Mo, Cd	Rb, Cr	ankerite	Ca(Fe++,Mg,Mn)(CO3)2
			quartz	SiO2
			dickit	Al2Si2O5(OH)4
			calcite	CaCO3
			pyrite	FeS2
			gypsum	CaSO4•2(H2O)
			talc	Mg3Si4O10(OH)2
			dolomite	CaMg(CO3)2
			quartz	SiO2
			sanidine	(K,Na)(Si,Al)4O8
			orthoclase	KAlSi3O8
			kaolinite	(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2•n(H2O)
			muscovite	Al2Si2O5(OH)4

5. CONCLUSIONS

The inorganic constituents of each of these deposits may be divided into detrital, biogenic, and authigenic minerals. The detrital material in oil shales is composed of mainly quartz, feldspars, certain clay minerals, and volcanic debris. Biogenic minerals are primarily amorphous, silica and calcium carbonate, however are not generally abundant. Authigenic minerals are pyrite and other metal sulfides, carbonates (calcite, dolomite, siderite), chert, phosphates, and saline minerals such as trona and halite. Authigenic minerals are important because they may provide information concerning redox conditions during or soon after the sedimentation process of the original solution, and climatic conditions (Shanks et. al. 1976).

Forest et al (1985) assert that enrichments of Ga, Rb, Cs, Sc, Ba, F, Be B, Cr, Th, Ta, Hf, Zr and rare earth elements occured especially in the detrital or clay minerals fraction with the major component. They also suggested that it may be caused by pyrite mineral of enrichment elements such as S, Co, Zn, As, Se, Mo, Sb, Pb and U. It showed high enrichment in V, Ni and Cu as well. Rubidium, Cs, Sc, Ga, Cr, La, Th, Ta, Hf and Zr enriched in the detrital fraction of the shale. Magnesium was more important in the clay minerals. Manganese concentration was correlated with calcite. Calcium, F, Ba, Sr and the rare earth elements correlated with phosphorus in these high phosphate samples, which indicated the presence of apatite.

In addition, Dunn (1974) suggested that the mineralogy of the samples is composed of organic matter, dolomite, calcite, illite, kaolinite, extremely fine-grained quartz, pyrite and rarely siderite. This significantly affects the geochemistry of trace element. Additionally, Mo, P, Cu and Ni was mostly associated elements with the clay minerals and the organic fraction, also Mn was associated with carbonate fraction. David et al.(1993) said that dissolution during catagenesis and diagenesis could provide componenet of minerals (such as Pb from feldispars) to enter in organic matter.

ÇOS in Hırka Formation was deposited primarily and generally as finely laminated, lacustrine sediments. Trona deposits have primary importance in Beypazarı Basin. Hırka Formation lithology is complex and variable. However, this formation generally consists of lacustrine shales and dolomitic marlstones, especially in rich oil shale zones.

Chemical composition of these minerals is presumed to contribute to the element enrichments. For example, when the depositional environment of ÇOS is interpreted, it is observed that the enrichment of Mn is caused by Ankerite, Kutnohorite and Alabandite minerals, the enrichment of Mg is caused by Dolomite, Ankerite, Magnesite, Spinel and Clay minerals, enrichment of Fe is caused by ankerite, talc, sepiolite, glauconite, pyrite, nantronit, kutnohorit, titanomagnetite biotite minerals. The results provide a definitive chemical and mineralogical characterization of the oil shale and identify the major mineralogical residences of the important trace elements.

Çayırhan Oil Shale is composed of detrital and authigenic clays, carbonates and silicates. The second (arid) climatic episode resulted in deposition of oil-rich marl. Besides the obvious economical value of oil produced from these deposits, a number of the associated authigenic minerals carry an economical potential as sources of trona, soda ash, zeolites, and other industrially important materials. In conclusion, mineral concent of the depositional environment have an impact upon the element enrichment.

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