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Factors controlling the paleo-sedimentary conditions of Çeltek oil shale, Sorgun-Yozgat/Turkey

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Research Article

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ABSTRACT

The study field covering an area of about 1000 km^2 is located in Sorgun town of the city of Yozgat. In the region Paleozoic, Campanian-Maastrichtian, Eocene, Miocene and Quaternary units are exposed. Among these units, the lower Eocene Çeltek formation hosts coal beds and oil shale. The Eocene epoch is important for organic matter deposition regarding oil and gas productivity and anoxic depositional conditions. In order to examine the paleo-sedimentary conditions of oil shales in the study area and their relation to Total Organic Carbon (TOC) contents and major-trace element contents, a total of 29 samples were collected from two boreholes and one Measured Stratigraphic Section (MSS). Samples have TOC contents varying from 1.97 to 16.17 wt% (average 6.30 wt%). The V/Cr, V/(V+Ni), U/Th, δU and Authigenic Uranium (AU) values of the Çeltek formation oil shales (ÇFOS) reveal that the oil shales have been deposited under variable paleo-environmental conditions. For paleo-salinity the Sr/Ba ratios indicate mostly deposition in a freshwater environment. Chemical Alteration Index (CIA) values and Sr/Cu ratios indicate that paleo-climate conditions of ÇFOS were dry, hot and occasionally humid. The Fe/Ti and (Fe+Mn)/Ti ratios reveal hydrothermal activity during sedimentation of oil shales. Zr/Rb ratios of samples are indicative of very weak paleo-hydrodynamics during the deposition of oil shales. Such variable geochemical conditions in the basin resulted in variable paleo-environmental conditions.

1. Introduction

Some trace elements behave in a sensitive manner under variable redox conditions; thus, they are very useful for the determination of the paleo-redox conditions in depositional environments (Calvert and Pedersen, 1993; Jones and Manning, 1994; Wignall, 1994; Crusius et al., 1996; Dean, 1993, 1997; Yarincik et al., 2000; Morford et al., 2001; Pailler et al., 2002). These trace elements are significantly accumulated in laminated organic-rich facies deposited under euxinic conditions. However, they are hardly ever found in bio-turbation and organic-poor facies.

There are several studies regarding the redox conditions during oil shale deposition and the relation between TOC content and redox-sensitive trace elements (Vine and Tourtelot, 1970; Holland, 1984; Robl and Barron, 1987; Özlük, 2010; Koca et al., 2010; Sarı et al., 2010; Koca, 2011; Yavuz Pehlivanlı, 2011; Sarı and Koca, 2012; Yavuz Pehlivanlı et al., 2013; Koralay and Sarı, 2013; Sarı et al., 2016).

For example, uranium exists as U^{6+}soluble under oxic-suboxic conditions and its enrichment is restricted to oxic environments (Calvert and Pedersen, 1993). Under anoxic conditions uranium is reduced to U^{4+}form. Under reducing conditions, uranium within the sediments forms ligands in the presence of humic acids and is enriched as uraninite (UO$_2$) at sediment-water interface (Klinkhammer and Palmer, 1991). Although reducing of U^{6+}is believed to be controlled by Fe redox reactions, the presence of H$_2$S may also give rise to sulfate reduction (Langmuir, 1978; Klinkhammer and Palmer, 1991; Zheng et al., 2002).

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Vanadium, nickel and cobalt are very important for determining the redox conditions of depositional environments. Under oxic conditions vanadium exists as V^{+5} in vanadate ions (Wehrli and Stumm, 1989). Humic and fulvic acids catalyze the reduction from vanadate to vanadyl (Templeton and Chasteen, 1980). Vanadium can be adsorbed as V^{4+} or transferred to the sediment as organometallic ligands (Morford and Emerson, 1999). Under extremely reducing conditions, e.g. in the presence of free H_2S, V is reduced to V^{3+}. Vanadium enters the medium in form of geo-porphyrine, solid oxide (V_2O_3) or hydroxide ($V(OH)_3$) (Breit and Wanty, 1991). Vanadium is reduced through a two-stage process which results in the formation of different V phases with different solubility under non-sulfidic anoxic versus euxinic conditions (Calvert and Pedersen, 1993).

Nickel generally occurs as Ni-carbonate ($NiCO_3$) or dissolved species accompanied by humic and fulvic acids (Achterberg et al., 1997). Under oxic conditions it occurs as Ni^{+2} or $NiCl^+$ ions (Calvert and Pedersen, 1993).The presence of organic compounds accelerates the transfer of Ni to the sedimentary environment and Ni is free in pore water at the sediment-water interface. Under anoxic conditions it may also be hold in pyrite as solid solution (Huerta-Diaz and Morse, 1992; Morse and Luther, 1999).

At oxic conditions cobalt may form compounds of dissolved cations (Co^{+2}) or humic and fulvic acids (Achterberg et al., 1997) and may exist as insoluble sulfide (CoS) at anoxic conditions (Huerta-Diaz and Morse, 1992). Moreover, since Co is slowly absorbed due to kinetic reasons, it is rarely found in authigenic sulfides (Morse and Luther, 1999).

Based on Ni/Co, V/Cr and V/(V+Ni) ratios the paleo-environmental conditions of organic-rich sedimentary rocks can be assessed (Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer, 2004). Li et al. (2018) reconstructed the paleo-environmental conditions through the V/Cr, V/(V+Ni), U/Th, δU and Authigenic Uranium (AU) values; the Sr/Ba ratio was used for paleo-salinity; paleo-climate data was used for Chemical Index of Alteration (CIA); and Sr/Cu ratios, Fe/Ti and (Fe+Mn)/Ti ratios for hydrothermal activity during sedimentation of oil shales, and Zr/Rb ratios for paleo-hydrodynamics.

The aim of this study is to examine the organic material abundance, the paleo-salinity, the paleo-climate, the hydrothermal conditions during deposition and the factors affecting the paleo-environmental characteristics (e.g. paleo-hydrodynamics) of oil shale samples obtained from Çeltek formation in the vicinity of Sorgun, Yozgat area, Central Turkey (Figure 1).

2. Geological Setting

The study area covering an area of about 1000 km^2 is located close to Sorgun town of the city of Yozgat (Figure 1). In the region Paleozoic, Campanian-Maastrichtian, Eocene, Miocene and Quaternary units crop out. The central Anatolian granitoids (Erler and Bayhan, 1993; Dönmez et al., 2005) are

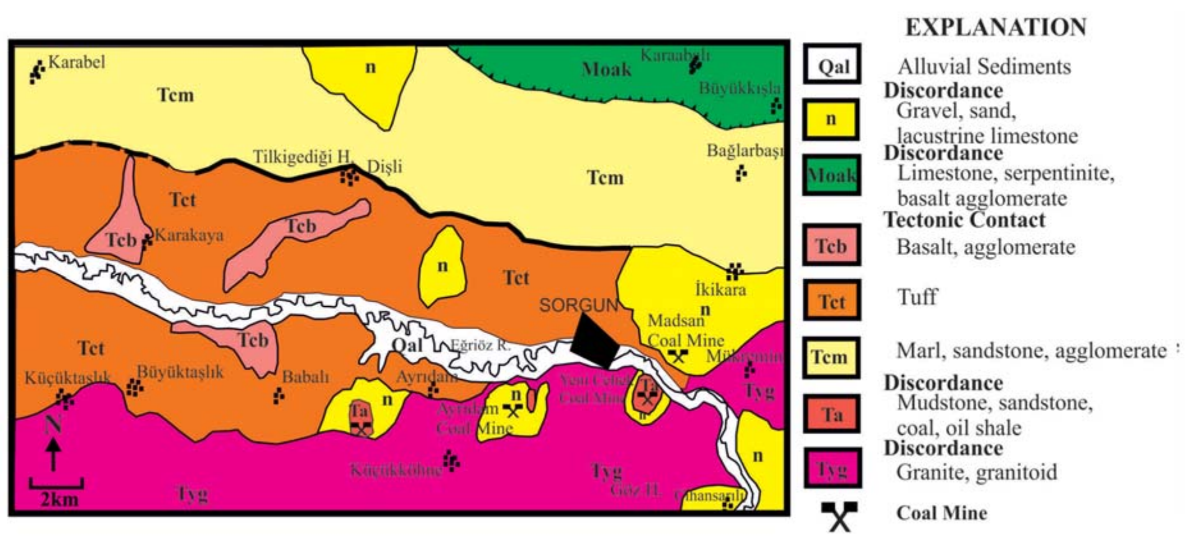

Figure 1- Geological map of the study area (Cicioğlu, 1995).

the oldest rock units around the study area which are unconformably overlain by the lower Eocene Çeltek formation composed of sandstone, coal, oil shale, lenticular sandstone and mudstone alternations (Cicioğlu, 1995). This formation is unconformably covered by the lower-middle Eocene Boğazköy formation starting with a basal conglomerate and continuing to the top with volcanic-interbedded sandstone, fossiliferous limestone, clay stone, clayey limestone, marl and various volcanic rocks including rhyolite, rhyolitic tuff, agglomerate, dacite, andesite and basalt. At the end of Lutetian ophiolitic rocks of the İzmir-Ankara-Erzincan suture zone were thrusted over the Boğazköy formation. All these units are overlain by Neogene deposits (Figures 1 and 2) (Cicioğlu, 1995; Beyazpirinç et al., 2014). The Kızılırmak formation, from bottom to the top consists of terrestrial conglomerate, sandstone, siltstone, claystone, mudstone and limestone (Beyazpirinç et al., 2014). It is covered by Anatolian granitoids and Plio-Quaternary units.

3. Material and Methods

Nineteen Çeltek formation oil-shale (ÇFOS) samples were collected from three different locations in the coal field of the Yeni Çeltek Coal Management in Sorgun: nine surface samples from a Measured Stratigraphic Section (MSS) (YÇ) and 10 samples from two cores (SJ and Ç). The samples from the MSS were taken systematically and the core samples were collected at 10 cm intervals per meter (Figure 3). Major and trace element contents were determined at the laboratories of the Bozok University. About 30 g of each sample was grinded to pass the 90 µm mesh. For trace and rare earth element contents 0.5 g sample was analyzed through ICP-ES (ICP emission spectrometry) and ICP-MS (ICP mass spectrometry) techniques at the Acme Analytical Laboratories Ltd (Canada). Moreover, the samples were analyzed using a Rock-Eval VI pyrolysis device at the Laboratories of the Turkish Petroleum Corporation (TPAO).

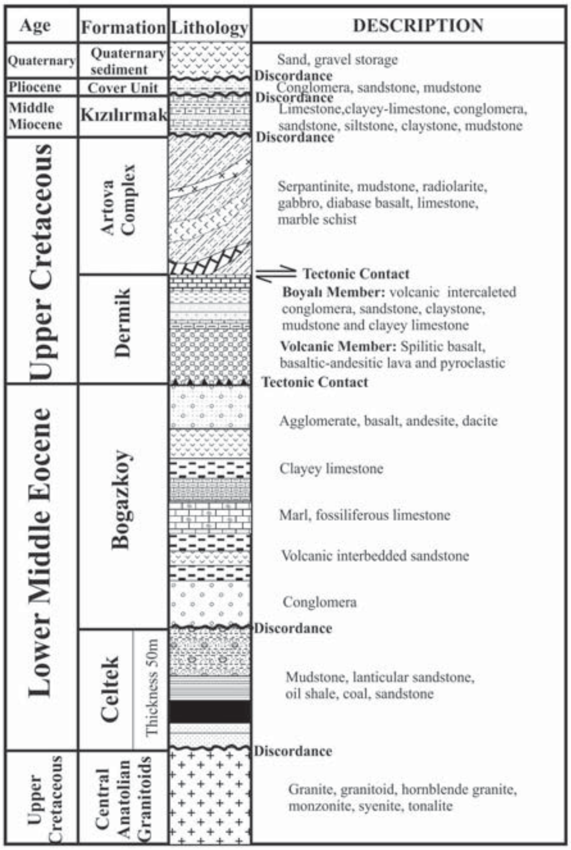

Figure 2- Generalized stratigraphic section of the study area of Sorgun basin (Modified from Beyazpirinç et al., 2014; Cicioğlu, 1995).

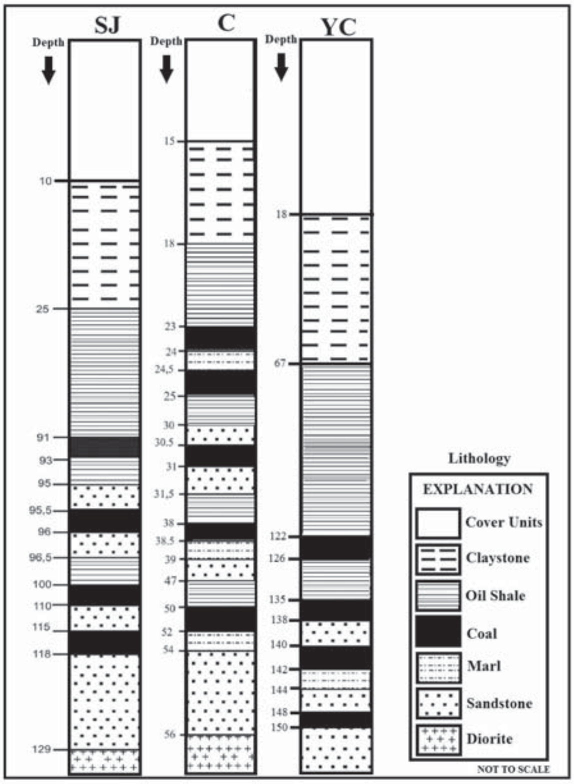

Figure 3- The lithological columns of the SJ and Ç cores and the YC Measured Stratigraphic Section (MSS) (not to scale).

4. Results and Discussion

4.1. Rock Eval Pyrolysis

The TOC (Total Organic Carbon) contents of oil shales range from 1.97 to 16.17 % with average of 6.30 %. The values show very good to prefect source rock character (Table 1).The HI-OI and HI-T_{max} diagrams indicate that the organic material consists of Type-1 and Type-2 kerogen (Figure 4a and b). Considering the T_{max} values (Table 2) and the kerogen types, the samples are generally within the oil window and depth-dependent variations of samples are indicative of immature to early mature stages (Espitalie et al., 1984).

Table 1- Source rock properties of ÇFOS based on Total Organic Carbon (TOC) content.

Peters and Cassa (1994)		Tissot and Welte (1984)		Jarvie (1991)		Sample	TOC (%)	Source Rock Quality
Corg (%)	Oil Potential	TOC (%)	Source Rock Quality	TOC (%)	Source Rock Quality			
0-0.5	Weak	0.1-0.5	Weak	0-0.5	Insufficient			
0.5-1	Middle	0.5-1	Middle	0.5-1	Middle	C	1.97-16.17	Good - Very Good
1-2	Good	1- 2	Good	>1	Enough	YC	2.14-14.85	Very Good
2- 4	Very good	2 - 10	Rich			SJ	2.48-3.13	Very Good

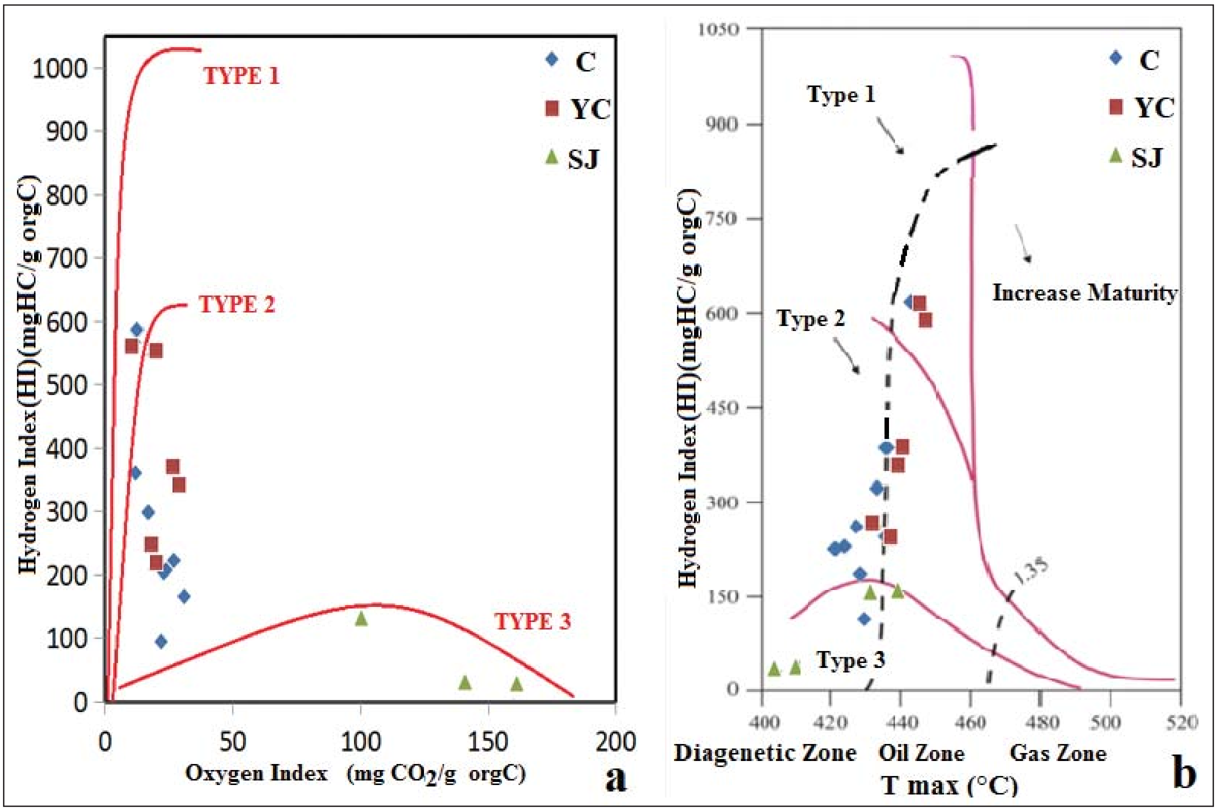

Figure 4 a- Characterization of organic matter in HI vs. OI diagram (Espitalie et al., 1977); b-Plot of Hydrogen Index (HI) vs. T_{max} of the ÇFOS samples (Mukhopadhyay et al., 1995).

Table 2- T_{max} limit values of ÇFOS according to kerogen types (Espitalie et al., 1984).

Type I	Type II	Type III	Degree of Maturation	Sample	TMAX (°C)
	<425 °C	<435 °C	Immature-Early Mature	C	418-436
440-448 °C	425-450 °C	435-465 °C	Oil window	YC	427-439
	>450 °C	>465 °C	Gas window	SJ	404-433

4.2. Elemental Composition

The distribution of major (>0.1 %), minor (between 100 ppm and 0.1%) and trace elements (<100 ppm) reflects the geochemical characteristics of the sediments. Although the use of element abundances is not the sole tool to determine the depositional conditions (Degens et al., 1958), all factors which are adsorbed from the water to organic and inorganic substances, which control the element contribution to the environment, are taken into consideration to figure out the paleo-environmental conditions. The enriched elements are retained within minerals or absorbed in organic material that formed in water at the immediate vicinity and are incorporated into authigenic minerals during or after the sedimentation (Cody, 1971).

In this study, all the samples evaluated are organic-rich oil shales. Major, trace elements and average concentrations of ÇFOS samples were computed (Tables 3 and 4).

4.3. Element Enrichments

Element enrichment of ÇFOS samples were computed on the basis of average shale values (Turekian and Wedepohl, 1961) using the equation:

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

Values >1 represent element enrichment whilst those <1 element depletion (Table 5). Results of calculations reveal that Si, Pb, U and As elements in almost all the samples show enrichment. It is noticeable that uranium appears enriched in all the elements with an enrichment factor varying from 1.19 to 153.7 (Table 5).

4.4. Paleo-environmental Conditions

The paleo-environmental conditions exert a great control on the preservation of organic matter (Li et al., 2018). Some redox-sensitive elements are used for determining the paleo-environmental conditions. In this study, some element ratios such as V/Cr, V/(V+Ni), U/Th, δU[dU=2U/(U+Th/3)] and authigenic uranium (AU=U-Th/3) were used to investigate the paleo-environmental conditions. V/Cr ratios > 4.25 are indicative of strong reducing conditions, those between 2 and 4.25 depict moderate reducing conditions and V/Cr ratios < 2 show oxidative conditions (Teng et al., 2004). V/(V+Ni) ratios > 0.5 are indicative of reducing conditions but ratios lower than this value depict oxidative conditions (Tribovillard et al., 2006). U/Th ratios > 1.25 are indicative of strong reducing conditions, those between 0.75 and 1.25 depict moderate reducing but ratios lower than this value represent oxidation (Ernst, 1970; Jones and Manning, 1994). δU values < 1 indicate oxidation and those > 1 depict reducing conditions (Zhao et al., 2016). AU values > 12 ppm are indicative of strong reducing conditions, those between 5-12 ppm moderate reducing conditions and values < 5 ppm represent oxidation (Deng and Qian, 1993; Teng et al., 2005).

Paleo-environmental assessment for ÇFOS samples based on these parameters are listed in table 6. The average V/Cr, V/(V+ Ni), U/Th, δU and AU values of ÇFOS samples are 3.32, 0.89, 0.61, 1.10 and 34.86, respectively (Table 6). Results of assessments and depth-dependent changes of V/Cr and U/Th reveal variable sedimentation processes and strong reducing to oxidative conditions (Figures 5 and 6).

4.5. Paleo-salinity

The Sr/Ba ratio is used to assess the paleo-salinity in the depositional environment. According to Wang and Wu (1983), Sr/Ba ratio> 1 is indicative of seawater influence, those between 1 and 0.6 depict brackish water and ratios < 0.6 represent freshwater conditions. The Sr/Ba ratios of ÇFOS samples are between 0.05 and 1.27 with a basin average of 0.57. These values indicate that the basin was mostly supplied with freshwater which was occasionally replaced by saline and brackish water (Table 6).

Table 3- Average main element contents (in %) of the ÇFOS samples from Sorgun Basin.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
C avr (n=10)	42.06	20.42	4.18	0.46	1.13	0.17	2.02	0.51	0.06	0.06	0.003
YC avr (n=9)	46.38	22.23	6.25	0.93	0.66	0.19	2.42	0.48	0.10	0.12	0.005
SJ avr (n=10)	59.94	13.72	4.63	1.28	4.73	1.14	3.91	0.52	0.10	0.06	0.005
ÇFOS Average	49.46	18.79	5.02	0.89	2.17	0.50	2.78	0.50	0.08	0.08	0.004

Table 4- Average trace element contents (in ppm) of the ÇFOS samples from Sorgun Basin.

Sample	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
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
ÇFOS Average	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- Elemental enrichment factors of ÇFOS samples in comparison to the World Shale Average (Turekian and Wedepohl, 1961).

According to Average Shale EF	Mn	Mg	Fe	Si	K	Ti	Ca	Na	**Pb**	Zr	P	Sr	Rb	**U**	Ba	Cu	Ni	**As**	V	Zn	Sb	Co	Mo	Cd
C5	0.75	0.24	0.42	**2.90**	0.85	0.74	0.62	0.31	**2.53**	**1.66**	0.31	0.73	**1.02**	**3.64**	0.89	0.26	0.08	**1.10**	0.40	0.67	0.17	0.51	0.08	0.28
C8	**2.27**	0.30	**1.33**	**3.24**	0.94	0.59	**2.40**	0.32	**2.97**	**1.47**	0.49	**1.48**	**1.09**	**5.68**	**1.21**	0.44	0.17	**3.82**	0.62	0.84	0.53	0.97	0.30	0.44
C10	0.27	0.23	0.70	**2.07**	0.54	0.52	0.16	0.10	**3.18**	0.76	0.55	0.58	0.81	**4.16**	0.52	0.46	0.18	**2.42**	0.50	**1.43**	0.38	0.64	0.15	0.67
C12	**1.19**	0.17	0.55	**2.15**	0.57	0.52	0.12	0.09	**2.46**	0.77	0.43	0.57	0.79	**2.65**	0.61	0.32	0.11	**1.98**	0.47	**1.41**	0.32	0.50	0.08	0.46
C19	0.37	0.15	0.43	**2.10**	0.57	0.61	0.08	0.07	**3.01**	0.90	0.20	0.52	0.81	**2.35**	0.60	0.29	0.11	**2.12**	0.46	0.57	0.21	0.54	0.06	0.21
C22	0.06	0.13	0.41	**2.89**	0.77	0.83	0.07	0.17	**3.49**	**2.08**	0.19	0.62	0.94	**2.92**	**1.00**	0.28	0.12	**1.71**	0.46	**1.33**	0.36	0.63	0.11	0.39
C28	0.03	0.07	0.14	**1.41**	0.22	0.44	0.06	0.02	**2.84**	0.42	0.15	0.36	0.67	**9.00**	0.21	0.34	0.01	0.28	0.21	0.13	0.34	0.04	0.20	0.07
C29	0.10	0.07	0.95	**1.27**	0.12	0.22	0.17	0.02	**19.69**	0.33	0.72	0.74	0.37	**85.78**	**7.34**	0.32	0.11	**3.99**	0.89	**2.22**	**1.97**	0.52	**1.07**	**2.15**
C32	0.07	0.07	0.41	**1.40**	0.25	0.49	0.09	0.02	**2.28**	0.60	0.05	0.40	0.66	**5.80**	0.22	0.15	0.03	**1.86**	0.32	0.29	0.29	0.23	0.33	0.15
C33b	0.04	0.06	0.16	**1.37**	0.18	0.38	0.07	0.02	**3.10**	0.30	0.10	0.34	0.54	**2.87**	0.18	0.26	0.03	**0.29**	0.33	0.19	0.14	0.15	0.27	0.17
YC2	0.05	0.08	0.46	**1.44**	0.21	0.40	0.07	0.02	**2.92**	0.32	0.17	0.27	0.57	**4.60**	0.20	0.36	0.05	**1.77**	0.44	**2.17**	0.36	0.77	0.70	0.67
YC5	**2.86**	0.32	**1.22**	**2.03**	0.52	0.60	0.32	0.06	**2.77**	0.88	0.51	0.50	0.74	**2.18**	0.55	0.26	0.09	0.97	0.46	0.71	0.20	0.50	0.07	0.25
YC6	0.48	0.16	0.39	**2.10**	0.54	0.56	0.11	0.06	**2.62**	0.82	0.41	0.47	0.79	**2.92**	0.54	0.32	0.13	**1.30**	0.47	0.75	0.26	0.55	0.11	0.32
YC7	0.18	0.19	0.52	**2.28**	0.59	0.55	0.15	0.08	**2.54**	0.87	0.65	0.56	0.82	**3.01**	0.61	0.42	0.11	**1.65**	0.49	**2.14**	0.20	0.99	0.14	0.99
YC10	0.36	0.28	0.52	**1.89**	0.53	0.41	0.14	0.11	**2.34**	0.39	0.58	0.32	0.72	**1.44**	0.36	0.62	0.20	**1.67**	0.73	0.59	0.29	0.77	0.16	0.21
YC12	0.56	0.32	0.74	**2.44**	0.56	0.39	0.17	0.08	**2.17**	0.46	0.43	0.48	0.80	**1.95**	0.47	0.39	0.15	**2.63**	0.69	0.71	0.20	0.56	0.33	0.25
YC13	0.84	0.26	0.63	**1.83**	0.51	0.39	0.12	0.09	**1.91**	0.40	0.32	0.38	0.74	**2.05**	0.37	0.45	0.12	**2.80**	0.68	0.68	0.21	0.42	0.28	0.21
YC14	0.64	0.35	0.56	**2.15**	0.59	0.50	0.12	0.27	**2.37**	0.45	0.28	0.42	0.79	**1.69**	0.42	0.51	0.13	**1.62**	0.73	**1.83**	0.22	0.43	0.18	0.33
YC15	0.17	0.35	0.70	**2.10**	0.59	0.44	0.13	0.13	**2.17**	0.42	0.51	0.43	0.82	**5.67**	0.41	0.59	0.21	**1.52**	0.74	0.51	0.09	**1.23**	0.12	0.56
SJ2	0.61	0.53	0.65	**4.69**	**1.42**	0.84	**3.16**	**1.11**	**1.49**	**1.60**	0.70	**1.67**	**1.37**	**1.78**	**1.94**	0.32	0.33	**1.12**	0.53	0.45	0.33	0.65	0.06	0.21
SJ4	**3.23**	**1.32**	**1.27**	**5.41**	**1.97**	0.70	**7.92**	0.25	**4.73**	**3.24**	0.74	**2.38**	**2.25**	**24.85**	**1.29**	0.42	0.22	**1.21**	0.76	**1.31**	0.45	**1.34**	0.05	0.28
SJ6	0.68	0.82	0.78	**3.92**	**1.35**	0.89	1.82	**1.58**	**2.51**	**1.49**	**1.03**	**1.49**	**1.55**	**23.10**	**1.65**	0.45	0.30	**2.44**	0.84	**1.05**	0.28	0.88	0.01	0.34
SJ8	**1.62**	0.74	0.94	**3.78**	**1.11**	**1.08**	**7.07**	**2.64**	**2.85**	**1.85**	**1.39**	**3.85**	**1.21**	**3.13**	**1.57**	0.23	0.18	**1.93**	0.74	0.61	0.53	**1.00**	0.01	0.44
SJ10	0.15	0.49	**1.09**	**3.02**	0.96	0.73	0.21	0.12	**3.25**	0.98	0.35	0.90	**1.47**	**9.62**	0.69	0.62	0.33	**6.90**	0.73	**1.96**	0.50	**1.12**	0.48	**1.25**
SJ12	0.07	0.37	0.55	**3.18**	0.96	0.72	0.17	0.18	**2.42**	**1.09**	0.28	0.90	**1.18**	**153.7**	0.74	0.66	0.17	**6.88**	0.71	0.82	**1.88**	0.64	**3.22**	0.59
SJ14	0.09	0.31	0.30	**5.97**	**1.54**	0.66	0.12	**1.03**	**1.19**	**1.41**	0.38	**1.36**	**1.49**	**5.32**	**1.67**	0.14	0.07	**4.87**	0.41	0.36	0.33	0.81	0.07	0.18
SJ16	0.18	0.43	**1.05**	**4.80**	**1.27**	0.92	0.13	0.62	**1.16**	**1.83**	0.28	**1.08**	**1.50**	**1.26**	**1.11**	0.30	0.09	**3.37**	0.77	0.54	0.59	0.55	0.04	0.17
SJ19	0.23	0.47	0.59	**3.78**	**1.62**	0.88	0.18	0.88	**1.51**	**1.55**	**1.09**	**1.58**	**1.67**	**2.11**	**2.13**	0.32	0.15	**1.79**	0.62	0.63	0.25	0.63	0.02	0.14
SJ22	0.17	0.54	0.55	**4.88**	**1.55**	0.71	0.17	**1.61**	**1.32**	**1.37**	0.78	**1.57**	**1.36**	**1.19**	**2.04**	0.20	0.07	**1.74**	0.38	0.53	0.28	0.61	0.01	0.16
ÇFOS Average	0.63	0.34	0.66	**2.84**	0.81	0.61	0.90	0.42	**3.10**	**1.06**	0.48	0.93	**1.02**	**12.98**	**1.09**	0.37	0.14	**2.34**	0.57	0.95	0.42	0.66	0.30	0.43
World Average Shale (Element/Al)	96.00	0.19	0.59	0.91	0.33	0.05	0.28	0.12	2.50	20.00	0.01	37.50	17.50	0.46	72.50	5.63	8.50	1.63	16.25	11.8	0.19	2.38	1.38	0.08

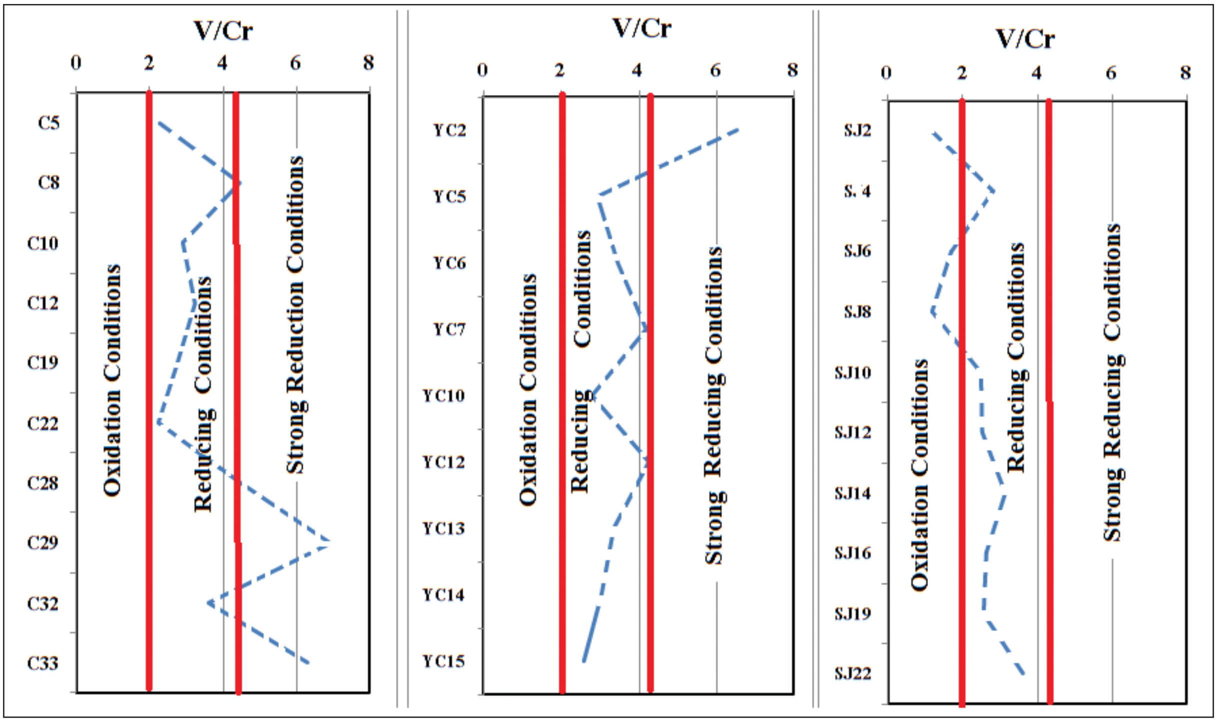

Figure 5- According to V / Cr ratios, Depth-dependent redox changes of ÇFOS.

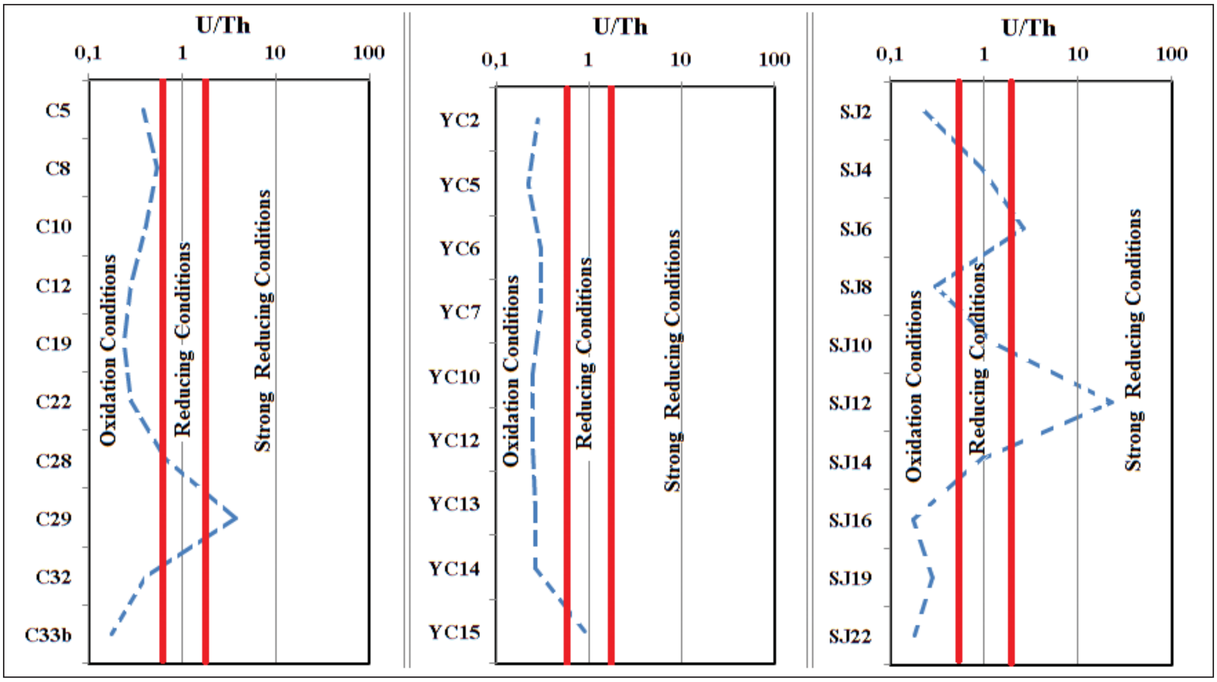

Figure 6- According to U/Th ratios, Depth-dependent redox changes of ÇFPS.

Table 6- The parameters characterizing the paleo-depositional environment of the ÇFOS samples.

Sample	V/Cr	V/(V +Ni)	U/Th	δU	AU	Sr/Ba	CIA	Sr/Cu	Fe/Ti	(Fe+ Mn)/Ti	Zr/Rb
C5	2.30	0.90	0.38	1.07	2.07	0.42	75.66	18.44	6.43	6.65	1.85
C8	4.46	0.87	0.54	1.23	6.07	0.63	58.84	22.34	24.97	25.82	1.54
C10	2.92	0.84	0.41	1.10	3.53	0.59	88.06	8.52	14.94	15.05	1.08
C12	3.25	0.89	0.28	0.91	-2.73	0.48	87.88	11.87	11.58	12.08	1.11
C19	2.75	0.89	0.24	0.83	-5.53	0.45	87.99	11.80	7.96	8.09	1.28
C22	2.25	0.88	0.28	0.92	-2.53	0.32	84.30	14.76	5.52	5.54	2.53
C28	4.46	0.97	0.65	1.32	35.00	0.87	94.70	6.96	3.43	3.45	0.72
C29	6.92	0.94	3.69	1.83	224.23	0.05	96.55	15.45	48.32	48.42	1.00
C32	3.62	0.95	0.41	1.10	4.40	0.97	93.34	18.29	9.36	9.39	1.05
C33b	6.31	0.95	0.18	0.69	-18.47	1.00	95.28	8.81	4.76	4.78	0.63
YC2	6.54	0.95	0.29	0.92	-4.17	0.69	94.88	5.04	12.92	12.94	0.65
YC5	2.96	0.91	0.22	0.80	-5.47	0.47	86.07	12.94	22.84	23.91	1.37
YC6	3.47	0.88	0.31	0.96	-1.47	0.45	88.79	9.83	7.75	7.94	1.18
YC7	4.19	0.89	0.31	0.96	-1.27	0.48	87.73	8.86	10.68	10.75	1.21
YC10	2.80	0.87	0.25	0.86	-2.90	0.46	88.61	3.46	14.00	14.19	0.61
YC12	4.28	0.90	0.25	0.85	-3.27	0.54	87.34	8.30	21.19	21.52	0.65
YC13	3.36	0.91	0.27	0.89	-3.07	0.53	88.46	5.62	18.15	18.63	0.61
YC14	3.05	0.91	0.26	0.88	-2.63	0.52	85.97	5.49	12.53	12.82	0.65
YC15	2.59	0.87	0.91	1.46	19.67	0.54	87.33	4.84	17.73	17.81	0.58
SJ2	1.15	0.76	0.23	0.82	-2.27	0.45	49.55	35.32	8.60	8.77	1.34
SJ4	2.83	0.87	0.97	1.49	35.33	0.96	32.98	37.38	20.16	21.18	1.64
SJ6	1.71	0.84	2.67	1.78	72.30	0.47	56.88	22.33	9.79	9.96	1.10
SJ8	1.19	0.89	0.30	0.95	-0.83	1.27	34.98	114.04	9.68	10.01	1.75
SJ10	2.48	0.81	1.33	1.60	28.57	0.68	80.30	9.71	16.67	16.72	0.76
SJ12	2.53	0.89		1.97	634.80	0.63	80.35	9.10	8.41	8.43	1.06
SJ14	3.14	0.92	0.90	1.46	10.07	0.42	70.16	66.42	4.97	5.00	1.08
SJ16	2.63	0.94	0.18	0.69	-3.70	0.51	74.64	24.02	12.62	12.66	1.40
SJ19	2.57	0.89	0.29	0.93	-1.37	0.38	70.51	33.06	7.38	7.43	1.06
SJ22	3.62	0.92	0.18	0.71	-3.50	0.40	67.92	52.12	8.58	8.63	1.15
ÇFOS Average	3.32	0.89	0.61	1.10	34.86	0.57	78.48	20.87	13.17	13.40	1.13

4.6. Paleo-climate

The climate generally affects mineral alteration, transport and source rock chemistry (Zhang et al., 2011).Thus, the Chemical Index of Alteration (CIA) may be modified by paleo-climate conditions (Bai et al., 2015). The CIA is computed from the equation CIA=100x[Al_2O_3/(Al_2O_3+CaO*+Na_2O+K_2O)] (Cox et al., 1995).

CIA values between 50 and 65 reflect cold and dry climate conditions during sedimentation. The values between 65 and 85 are indicative of a warm and humid climate regime. If CIA is in the range of 85 to 100, the climate is hot and humid. CIA values of ÇFOS samples vary from 32.98 to 96.55 and the basin average is 78.48 (Table 6). These values show that the paleo-climatic conditions change from cold to dry and hot to humid conditions from time to time, but the environment may have been generally hot and humid.

The Sr/Cu ratios are also informative for paleo-climate conditions. Sr/Cu ratios of 1.3 to 5.0 reflect hot and humid climate regime whilst ratios >5 are indicative of dry and hot conditions (Liang et al., 2015). The Sr/Cu values of ÇFOS samples vary from 3.46 to 114.04 and basin average is 20.87. These findings imply paleo-climate conditions show dry and hot and occasionally hot-humid environment (Table 6).

4.7. Hydrothermal Depositional Conditions

Sediments associated with hydrothermal fluids are called hydrothermal deposits (Zhong et al., 2015). Hydrothermal fluids exert a great control on trace element concentrations and the abundance of organic material accumulated in sedimentary rocks (Chu et al., 2016). The Fe/Ti and (Fe+Mn)/Ti ratios reflect a hydrothermal contribution to the sediments (Li et al., 2018). Fe/Ti ratios >20 and (Fe+Mn)/Ti ratios of 20±5 show hydrothermal interaction with the sediments (Boström,1983). Fe/Ti and (Fe+Mn)/Ti ratios of ÇFOS samplesreveal that hydrothermal fluids occasionally contributed to element enrichment during sedimentation (Table 6).

4.8. Paleo-hydrodynamics

Zircon is typically deposited in terrestrial and shallow marine environments. Due to its active chemical properties, Rb is likely transported and accumulated in deep water (Teng et al., 2005). Therefore, Zr/Rb can be used for the assessment of changes in water depth. Lower Zr/Rb ratios are a result of deeper sedimentary water circulation and weaker hydrodynamic forces. It is suggested that Zr/Rb ratio of around 0.92 represents weak hydrodynamic forces whilst higher ratios from 1.25 to 4.76 are indicative of an environment with strong paleo-hydrodynamic forces (Teng, 2004; Zhao et al., 2016). The Zr/Rb ratios of ÇFOS samples vary from 0.58 to 2.53 and basin average is 1.13. These values imply that both weak and strong hydrodynamic prevailed from time to time during the sedimentation in the basin (Table 6).

4.9. Factors Controlling the Paleo-environmental Conditions During the Total Organic Carbon (TOC) in Oil Shales

Paleo-environmental data (V/Cr, V/(V+Ni), U/Th, δU, authigenic uranium (AU), Sr/Ba, CIA, Sr/Cu, Fe/Ti, (Fe+Mn)/Ti and Zr/Rb ratios) of the ÇFOS samples were correlated on an individual basis with the total organic carbon (TOC) contents of oil shales (Figure 7a-k). Samples collected from different locations and

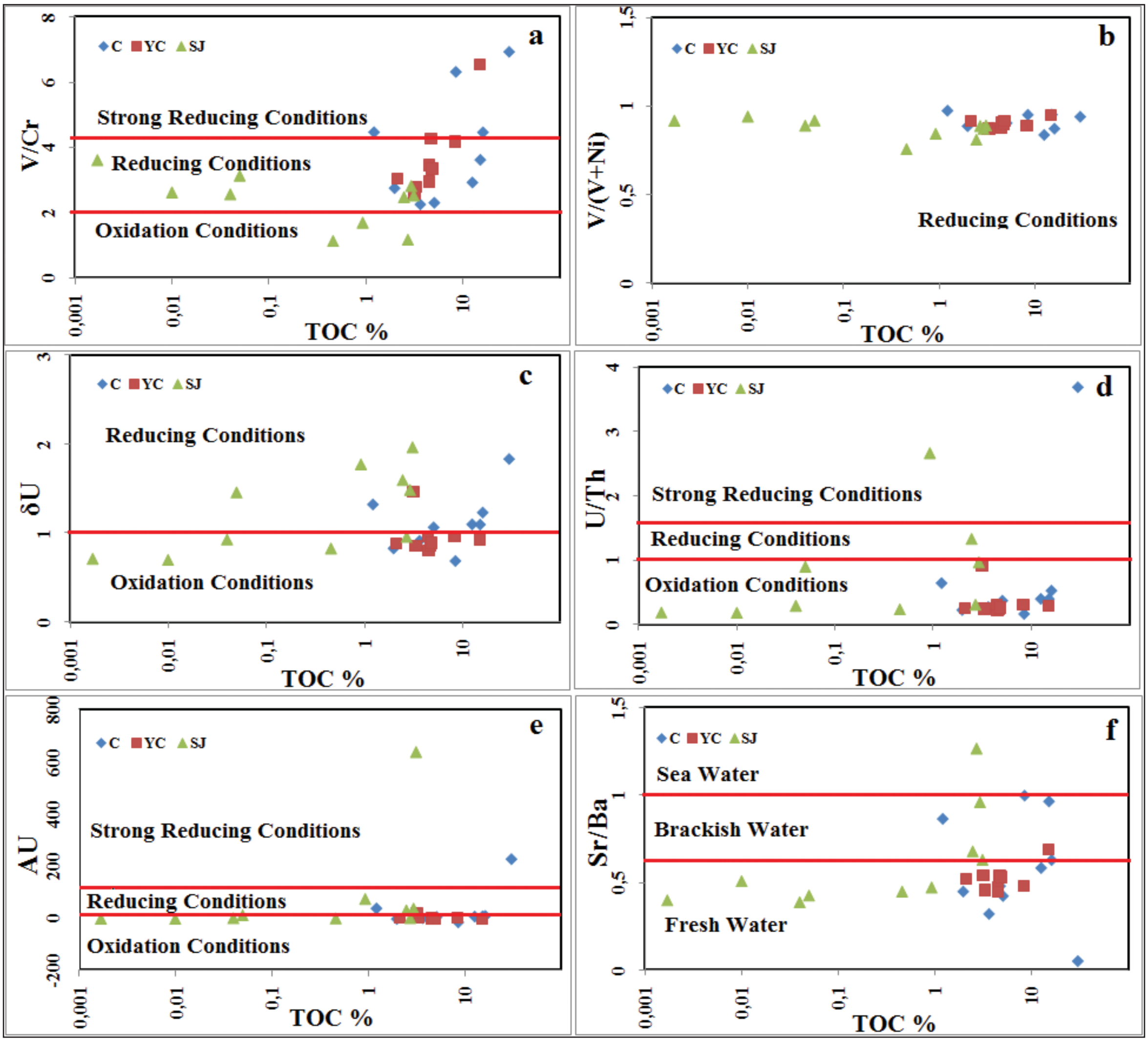

Figure 7- Correlation diagrams of TOC (%) versus parameters of the depositionalpaleo-environment: (a) V/Cr, b) V/(V + Ni), c) δU, d) U/Th, e) Authigenic Uranium (AU), f) Sr/Ba ratios, g) Chemical Index of Alteration (CIA), h) Sr/Cu, i) Fe/Ti, j) (Fe + Mn)/Ti and, k) Zr/Rb of ÇFOS samples (Li et al., 2018).

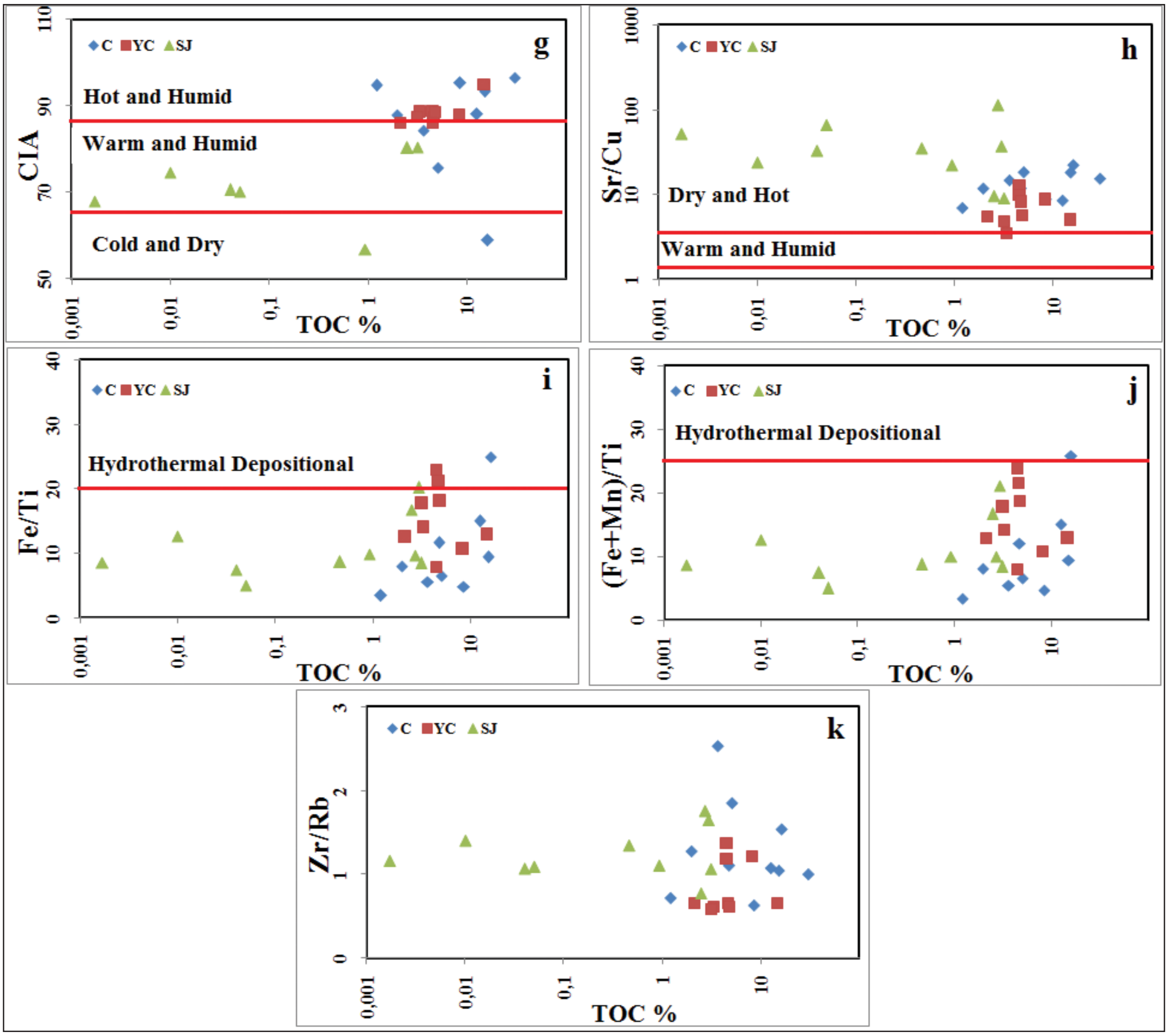

Figure 7- continued.

depths are differently correlated with TOC. Figure 7 reveals that V/Cr (a), CIA (g), Sr/Ba (f), Fe/Ti (i) and (Fe+Mn)/Ti (j) ratios have positive correlation with TOC. The data shows that element characteristics of ÇFOS samples are consistent with the preservation of organic material and high reducing conditions.

5. Conclusions

In this study the conditions dominating during the formation of the oil shales hosted in the Çeltek formation (ÇFOS), are assessed. The samples have TOC values varying from 1.97 to 16.17 wt% (average 6.30 wt%) revealing a very good source rock. The T_{max} values indicate that in respect of the oil window the samples are at immature-early mature stage. Considering the average values of the world shales provided by Turekian and Wedepohl (1961), Si, Pb, U and As reveal enrichment at all sampling locations. Under oxic-suboxic conditions uranium exists as soluble U^{6+} which necessitates the restriction of uranium enrichment to oxic environments. However, as shown from Figure 6, high uranium enrichment is consistent with strong reducing conditions.

Geochemical data of the ÇFOS samples (e.g. V/Cr, V/(V+Ni), U/Th, δU and AU (authigenic uranium)) indicate that the oil shales were deposited under variable paleo-environmental conditions. The Sr/Ba ratios point to deposition in a freshwater environment. The paleo-climatic data of ÇFOS samples show that when the chemical change index (CIA) and Sr / Cu ratios are evaluated, there are sedimentation environments ranging from dry-hot climate to hot-humid climate. Chemical weathering typically increases as temperatures rise and rain falls, which means rocks in hot and wet climates experience faster rates of chemical weathering than do rocks in cold, dry climates. The Fe/Ti and (Fe+Mn)/Ti ratios reflect hydrothermal contribution during the sedimentation of oil shales. According to the Zr/Rb ratios, weak paleo-hydrodynamics prevailed during deposition. The relations between TOC and redox element ratios indicate that the paleo-environmental conditions exerted a great control on the deposition of organic matter. The studied oil shale samples point to variable redox conditions and therefore, water chemistry, environment-climate conditions and organic productivity on the lake surface must have also varied.

The paleo-climatic data of ÇFOS samples show that when the chemical change index (CIA) and Sr / Cu ratios are evaluated, there is precipitation from dry-hot environments to hot-humid environments.

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References

Achterberg, E. P., Van Den Berg, C. M. G., Boussemart, M., Davison W. 1997. Speciation and Cycling of Trace Metals in Esthwaite Water: A Productive English Lake With Seasonal Deep-Water Anoxia. Geochim. Cosmochim. Acta,Vol. 61, pp. 5233–5253.

Bai, Y., Liu, Z., Sun, P., Liu R., Hu, X., Zhao, H., Xu, Y. 2015. Rare earth and major element geochemistry of Eocene fine-grained sediments in oil shale- and coal-bearing layers of the Meihe Basin, Northeast China. J Asian Earth Sci., 97, Vol., 97, pp. 89–101.

Beyazpirinç, M., Akçay, A.E., Tarhan, N., Sönmez, M.K., Havzoğlu, T., Bilgiç, T., Bademler, F., Ünal, M. 2014. Akdağmadeni masifi nin jeolojisi ve jeodinamik evrimi projesi 2011-2012 yıllarına ait ara rapor. Maden Tetkik ve Arama Genel Müdürlüğü Rapor No: 11763, Ankara (unpublished).

Boström, K. 1983. Genesis of ferromanganese deposits-diagnostic criteria for recent and old deposits. Hydrothermal Processes at Seafloor Spreading Centers, Springer, Berlin, pp 473–489

Breit, G. N., Wanty, R. B. 1991. Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. Chemical Geology, Vol. 91, pp. 83-97.

Brumsack, H. J. 2006. The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation; Palaeogeography, Palaeoclimatology, Palaeoecology, Vol. 232, pp. 344–361.

Calvert, S. E., Pedersen, T. F. 1993. Geochemistry of Recent oxic and anoxic marine sediments: implications for the geological record. Marine Geology, Vol. 113, pp. 67-88.

Cicioğlu, E. 1995. Sorgun (Yozgat) Kömürlerinin Kimyasal ve Petrografik Özelliklerinin İncelenmesi,Yüksek Lisans Tezi, Hacettepe Üniversitesi, Ankara.

Chu, C. L., Chen, Q. L., Zhang, B., Shi, Z., Jiang, H. J., Yang, X. 2016. Influence on formation of Yuertusi Source Rock by hydrothermal activities at Dongergou section, Tarim Basin. Acta Sedimentol Sin., 34, Vol. 4, pp. 803–810.

Cody, R. D. 1971. Adsorption and the reliability of trace elements as environmental indicators for shales. J. Sediment. Petrol., Vol. 41, pp. 461-471.

Cox, R., Lowe, D. R., Cullers, R. L. 1995. The influence of sediment recycling and Basement Composition of Evolution of Mudrock Chemistry in the Southwestern United States. Geochim Cosmochim Acta, 59, Vol. 14, pp. 2919–2940.

Crusius, J., Calvert, S., Pedersen, T., Sage, D. 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth Planet Science Letter, Amsterdam, Vol. 145, pp. 65–78.

Dean, W. E. 1993. Physical properties, mineralogy, and geochemistry of Holocene varved sediments from Elk Lake, Minnesota. In Bradbury J. P., W. E. Dean (eds.), Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States. Geol. Soc. America Spec. Paper 276, Boulder (CO), pp. 135–157.

Dean, W. E. 1997. Rates, timing, and cyclicity of Holocene eolian activity in north-central United States: Evidence from varved lake sediments. Geology, Vol. 25, pp. 331–334.

Degens, E. T., Williams, E. G., Keith, M. L. 1958. Environmental studies of carboniferous sediments: part II. Application of geochemical criteria. Bull J Immunol. Vol. 42, pp. 981–997.

Deng, H. W., Qian, K. 1993. Sedimentary geochemistry and environmental analysis. Gansu Science And Technology Press, Gansu (in Chinese).

Dönmez, M., Bilgin, Z. R., Akçay, A. E., Kara, H., Yergök, A. F., Esentürk, K. 2005. Türkiye Jeoloji Haritaları, Kırşehir-İ31 Paftası, No: 46, Maden Tetkik ve Arama Genel Müdürlüğü Yayını, Ankara.

Erler, A., Bayhan, H. 1993. Orta Anadolu Granotoidleri, Hacettepe Üniversitesi, Yer Bilimleri 25. Yıl Sempozyumu, Tebliğ, 20. Sayfa, Ankara.

Ernst, T. 1970. Geochemical Facieses Analysis, Elsevier, Amsterdam, pp. 152.

Espitalie, J., Madec, M., Tissot, B., Mennig, J.J., Leplat, P. 1977. Source rock characterization method for exploration: Proceedings, Ninth Annual Offshore Technology Conference, Vol. 3, p. 439-444.

Espitalie, J., Marquis, F., Borsony, I. 1984. Geochemical logging, in Voorhees, K. J., ed., Analytical pyrolysis: London, Butterworth and Co., Ltd., p. 276-304.

Hatch, J. R., Leventhal, J. S. 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A. Chemical Geology, Vol. 99, pp. 65–82.

Holland, H. D. 1984. The Chemical Evolution of the Atmosphere and the Oceans. Princeton University Press, 598 pp.

Huerta-Diaz, M. A., Morse, J. W. 1992. Pyritization of trace metals in anoxic marine sediments. Geochim. Cosmochim. Acta., Vol. 56, pp. 2681-2702.

Jarvie, D. M. 1991. Total Organic Carbon TOC Analysis. Merrill, R. K., ed., Source and Migration Processesand Evaluation Techniques, Tulsa, American Association of Petroleum Geologists, pp. 113-118.

Jones, B., Manning, D.A.C. 1994. Comparison of geochemical indices used for the interpretation of depositional environments in ancient mudstones. Chem Geol. 111, Vol. 1–4, pp. 112–129.

Klinkhammer, G.P., Palmer, M.R. 1991. Uranium in the oceans: Where it goes and why. Geochimica et Cosmochimica Acta, Vol. 55, pp. 1799-1806.

Koca, D. 2011. Nallıhan (Ankara, Türkiye) civarı bitümlü şeyllerinde organik madde ve iz element zenginleşmeleri. Ankara Üniversitesi Fen Bilimleri Enstitüsü Jeoloji Mühendisliği Anabilim Dalı, Doktora tezi, pp.392.

Koca, D., Sarı, A., Engin, H., Koç, Ş., Yavuz, B. 2010. Şeyl türü kayaçların (Tekirler-Nallıhan/Ankara) redoks depolanma koşulları. 35. Yıl Jeoloji Sempozyumu, s. 111-112, 4-7 Ekim 2010, Konya.

Koralay, D. B., Sarı, A. 2013. Redox Conditions and Metal-Organic Carbon Relations of Eocene Bituminous Shales (Veliler/Mengen-Bolu/Turkey). Energy Sources, Part A, Vol., 35, pp.1597-1607.

Langmuir, D. 1978. Uranium solution metal equilibra at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta, Vol. 42, pp. 547-569.

Li, D., Li, R., Zhu, Z., Xu, F. 2018. Elemental characteristics of lacustrine oil shale and its controlling factors of palaeo-sedimentary environment on oil yield: a case from Chang 7 oil layer of Triassic Yanchang Formation in southern Ordos Basin. Acta Geochim, Vol. 37, 2, pp. 228–243.

Liang, W. J., Xiao, C. T., Xiao, K., Lin, W. 2015. The relationship of Late Jurassic paleoenvironment and paleoclimate with geochemical elements in Amdo Country of northern Tibet. Geol China, 42, Vol. 4, pp.1079–1091 (in Chinese with English abstract)

Morford, J. L., Emerson, S. 1999. The geochemistry of redox sensitive trace metals in sediments. Geochimicaet Cosmochimica Acta, Vol. 63, pp. 1735-1750.

Morford, J. L., Russell, A. D., Emerson, S. 2001. Trace metal evidence for changes in the redox environment associated vvith the transition from terrigenous clay to diatomaceous sediment, Saanich inlet, B. C. Marine Geology, Vol. 174, pp. 355-369.

Morse, J. W., Luther, G.W. 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. Geochimica et Cosmochimica Acta, Vol. 63, pp. 3373-3378.

Mukhopadhyay, P. K., Wade, J. A., Kruge, M. A. 1995. Organic Facies and Maturation of Jurassic/Cretaceous Rocks and Possible Oil-Source Rock Corelation Based on Pyrolysis of Asphaltenes, Scotion Basin, Canada. Organic Geochemistry, Vol. 221, pp. 85-104.

Özlük, M. 2010. Himmetoğlu Formasyonu (Bolu) Bitümlü Şeyllerinde Organik Karbon ve Cr, Fe, Mo, Mn ve V Elementlerinin İlişkilerinin İncelenmesi. Ankara Üniversitesi FBE, Jeoloji Mühendisliği ABD. Yüksek Lisans tezi 109s.

Pailler, D., Bard, E., Rostek, F., Zheng, Y., Mortlock, R., Geen, A. 2002. Burial of redox-sensitive metals and organic matter in the equatorial Indian Ocean linked to precession. Geochimica et Cosmochimica Acta, Vol. 66, pp. 849-865.

Peters, K. E., Cassa, M. R. 1994. Applied source rock geochemistry. In: The petroleum system- from source to trap, L. B. Magoon and W. G. Dows eds., AAPG, Vol. 60, pp. 93-117.

Rimmer, S. M. 2004. Geochemical paleoredox indicators in the Devonian Mississippian black shales, Central Appalachian Basin USA. Chemical Geology, Vol. 206, pp. 373-391.

Robl,T. L., Barron, L. S. 1987. The geochemistry of black shales in central Kentucky and its relationship to inter-basinal correlation and depositional environment. In: McMillan ,A. F., Embry, A. F., Glass, D. G.(Eds.), Devonian of the World, Vol.II: Sedimentation. Mem. Can. Soc. Pet.Geol., Vol.14, pp.377-396.

Sarı, A., Koca, D. 2012. Jura - Kretase yaşlı Akkuyu Formasyonunun (Orta Toroslar/ Türkiye) provenans, tektonik ve redoks koşullarına bir yaklaşım. Maden Tetkik ve Arama Dergisi, Sayı 144, S.51-73.

Sarı, A., Yavuz Pehlivanlı, B., Koca, D., Koç, Ş. 2010. During Triassic Paleoredox and Provenance Investigation of Rich Organic Matter Tarasçı Formation (Middle Taurus/Turkey), Elec Lett Sci Eng, Vol. 6, pp. 9-24.

Sarı, A., Akkaya, P., Özakar, E. 2016. Kürnüç/Göynük-Bolu Alt Eosen Bitümlü Kayaçlarının Depolanma Ortamı ve Organik Jeokimyasal Karakteristikleri. Maden Tetkik ve Arama Dergisi, Sayı 152, S. 1-17.

Templeton, G. D., Chasteen, N. D. 1980. Vanadium–fulvic acid chemistry conformational and binding studies by electron spin probe techniques. Geochim. Cosmochim. Acta, Vol. 44, pp. 741.

Teng, G. E, 2004. The Distribution of elements, carbon and oxygen isotopes on Marine Strata and environmental correlation between they and hydrocarbon source rocks formation an example from Ordovician Basin, China. Graduate School of Chinese Academy of Sciences (Lanzhou Institute of Geology), Lanzhou.

Teng, G. E., Liu, W. H., Xu, Y. C., Chen, J. F. 2004. Identification of effective source rocks of Ordovician marine sediments in Ordos Basin. Prog Nat Sci., 14, Vol. 11, pp. 1249–1252 (in Chinese).

Teng, G. E., Hui, L. W., Xu, Y. C., Chen, J. F. 2005. Correlative study on parameters of inorganic geochemistry and hydrocarbon source rocks formative environment. Adv Earth Sci., 20, Vol. 2, pp.193-200

Tissot, B., Welte, D. H. 1984. Petroleum formation and occurrence: 2. edition Springer-Verlag, Berlin, pp. 699.

Tribovillard, N., Algeo, T. J., Lyons, T., Riboulleau, A. 2006. Trace metals as paleoredox and paleoproductivity proxies an update. Chem Geol, 232, Vol. 1–2, pp.12–32.

Turekian, K. K., Wedepohl, K. H. 1961. Distribution of the elements in some major units of the Earth's crust. Bull. Geol. Soc. America, 72, Vol. 2, pp. 175-192

Vine, J., Tourtelot, E. 1970. Geochemistry of black shale deposits a summary report. Econ. Geo., Vol. 65, pp. 253-272.

Wang, Y. Y., Wu, P. 1983. Geochemical criteria of sediments in the coastal area of Jiangsu and Zhejiang Provinces. J Tongji Univ (Nat Sci), Vol. 4, pp.82–90 (in Chinese with English abstract)

Wehrli, B., Stumm, W. 1989. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. Geochim. Cosmochim. Acta, Vol. 53, pp. 69–77.

Wignall, P. B. 1994. Black Shales. Oxford Monographs on Geology and Geophysics No. 30, Oxford Scientific Publications, Oxford, U.K., pp.127.

Yarincik, K. M., Murray, R. W., Lyons, T. W., Peterson, L.C., Haug, G.H. 2000. Oxygenation history of bottom waters in the Cariaco Basin, Venezuela, over the past 578,000 years: results from redox-sensitive metals (Mo, V, Mn, and Fe) Paleoceanography, 15, Vol. 6, pp.593–604. doi:10.1029/1999PA000401.

Yavuz Pehlivanlı, B. 2011. Hırka Formasyonu (Beypazarı, Ankara, Türkiye) Bitümlü şeyllerinin İnorganik element depolanmaları ve organik-inorganik elementler arasındaki kökensel ilişkiler. Ankara Üniversitesi Fen Bilimleri Enstitüsü Jeoloji Mühendisliği Anabilim Dalı, Doktora tezi, pp. 550.

Yavuz Pehlivanlı, B., Koç, Ş., Sarı, A. 2013. Geochemical Paleoredox Variations Dependent upon Depth of Samples Contain Rich Organic Matter in Hırka Formation, Beypazarı-Ankara, Turkey", 33rd Oil Shale Symposium, October 14-18 2013. Colorado School of Mines Golden Colorado, USA. 49. p.

Zhang, C. L., Gao, A. L., Liu, Z., Huang, J., Yang, Y. J., Zhang, Y. 2011. Study of character on sedimentary water and Palaeoclimate for Chang 7 oil layer in Ordos Basin. Nat Gas Geosci, 22, Vol. 4, 582–587 (in Chinese with English abstract).

Zhao, B. S., Li, R. X., Wang, X. Z., Wu, X. Y., Wang, N., Qin, X. L., Cheng, J. H., Li, J. J. 2016. Sedimentary environment and preservation conditions of organic matter analysis of Shanxi formation mud shale in Yanchang exporation area, Ordos Basin. Geol Sci Technol Inf 35, Vol. 6, pp.103–111 (in Chinese with English abstract).

Zheng, Y., Anderson, R. F., Van Geen, A., Fleischer, M. Q. 2002. Remobilization of authigenic uranium in marinesediments by bioturbation. Geochimica et Cosmochimica Acta, Vol. 66, pp. 1759-1772.

Zhong, D. K., Jiang, Z. K., Guo, Q., Sun, H. T. 2015. A review about research history, situation and prospects of hydrothermal sedimentation. Palaeogeogr 17, Vol. 3, 285–296 (in Chinese with English abstract).