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ELEMENT ENRICHMENTS IN BITUMINOUS ROCKS, HATILDAĞ FIELD, GÖYNÜK/BOLU

Ali SARI[a*], Murad ÇİLSAL[b] and Şükrü KOÇ[a]

[a] *Ankara Üniversitesi Müh.Fak., Jeoloji Müh.Böl., 06100 Tandoğan/Ankara*
[b] *Ankara Üniversitesi Fen Bilimleri Enstitüsü Müdürlüğü İrfan Baştuğ Caddesi, 06110 Dışkapı/ANKARA*

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C_{org}, Element Enrichment, Redox, Oxic, Suboxic, Anoxic, Sulfidic Environment.

ABSTRACT

In this study, element enrichments in bituminous rocks (bituminous shale, bituminous clays- tone and bituminous marl) of the Kabalar formation in the Hatıldağ field in Göynük town of the city of Bolu are investigated and their economic potential is discussed with regard to being a mineral deposit. Element analysis was conducted with ICP-ES (ICP emission spectrometry) and ICP-MS (ICP mass spectrometry) techniques. Organic carbon content in rocks was analyzed with Rock-Eval VI device. In pyrolysis analysis conducted on a total of 28 bituminous rocks that are collected from the Kayalık Dere measured stratigraphic section, Corg minimum and maximum are 0.40 %wt and 8.25 %wt, respectively (with average of 3,6 %wt). Major and trace elements analyzed were compared with those of Peru Continental Shelf Sediments, Namibia Continental Shelf Sediments, Gulf of California Sediments, Me- diterranean Sapropels, Black Sea Sapropels, Cenomanian/Turonian (C/T) Demerara Rise Anoxic Sediments and C/T Gubbio Anoxic Sediments which are known to be deposited under anoxic conditions. In the studied samples, enrichment levels of major and trace element con- tents are determined with respect to average shale. Fe, Mg, Ca and K of the major elements and As, Ba, Co, Cu, Ni, Rb, Sr, V, Zn and Zr of trace elements were found to be more enriched with respect to basins compared. Higher concentrations of Ca, Mg and Ba elements in the studied samples indicate that depositional environment in Hatıldağ is more carbonaceous and suboxic.

1. Introduction

The study area is located between Dağhacılar and Kabalar villages within boundaries of Göynük town, Bolu. In the field, Paleocene-Eocene units are exposed. Bituminous rocks cropping out in the study area are quite thick, reaching 290 meter in some places. This situation increases the economic value of the region in terms of petroleum and gas potential. It is also significant since these rocks accumulate plenty of major, trace and rare earth elements.

Some of the studies related to general geology, coal geology and bituminous shales are as follows; Şeker and Kesgin, 1991; Sarı and Sonel, 1995; Şener and Şengüler, 1998; Büyükutku et al., 2005; Sarı and Aliyev, 2005; Aliyev, et al., 2006; Sarı et al., 2007, Kara and Korkmaz, 2008; Şengüler, 2012.

The organic rocks, which are the source of today's oil deposits, were deposited in mild periods of the world history that correspond to Cambrian- late Devonian-Carboniferous, middle late Permian and

* *Corresponding author: Ali Sarı, sari@eng.ankara.edu.tr*

Cretaceous times. Bituminous rocks are deposited in much sulfurous, reducing environment, which was formed as a result of high organic productivity developing in the basin, and due to accumulation and decay of dead organisms at the bottom. In studies, it was seen that there was a systematical relationship between these bituminous rocks and the element enrichment. It was also observed that much sulfurous reducing environmental conditions that formed as a result of the accumulation and decay of dead organism at the bottom had the most significant role in element enrichments. Free metals in sulfidic environments are either bonded to an organic structure or deposited as metal sulfites and enriched in bituminous rocks. Metals that are taken into river bodies as the river flows into basin and detaches them from rocks, dissolved metals in sea water, hydrothermal solutions that comes from faults and fractures or volcanic ashes are shown as the source of metals in bituminous rocks (Mao et al., 2002; Cruse and Lyons, 2004).

The increasing oil prices in the world have forced the USA and other countries to find new sources for alternative energy within last 15 years. The need for the alternative energy have revived bituminous rocks (bituminous shale, bituminous marl and bituminous claystone) in recent years. Within this scope, the shale gas exploration, which takes important place in the agenda of big countries such as; the USA and China, have accelerated investigations in Turkey as well. In doing so; the fracturing process in Silurian Dadaş Formation of Shell Company in Diyarbakır has been completed and test studies are performed for production. Again, the oil production studies from bituminous rocks still continue in Hatıldağ/ Göynük field within scope of a joint project which is carried out by Turkish Coal Enterprises (TKİ) and Turkish Petroleum Corporation (TPAO). It is especially possible to enrich elements from organic rich rocks using residual ashes which remain after retorting the oil at the surface. Bituminous rocks within this framework are very rich storage for Major, Trace and Rare Earth Elements (REE) and assessed like a mineral deposit. In near future, the source supply for elements, which will be needed by high technologies, will be spoken in the agenda of Turkey. When looking from these points of views, this investigation is important for element acquirements and source determinations. Remarkable enrichments in Si, Mn, Cr, Fe, Na, K, Ca, Mg and Ti elements and depletion in P element were observed in bituminous samples of Kayalık Stream measured stratigraphical section (MSS) in this study. Among trace elements, the enrichments of Ni, Sc, Ba, Be, Co, Cs, Hf, Sn, Sr, U, Th, Ta, V, W, Cu, Pb, As, Sb, Ag, and Se elements are generally in higher concentrations than average shale.

2. Material and Method

Bituminous rocks (bituminous shale, bituminous marl and bituminous shale) used in this study were taken from Kayalık Stream in Hatıldağ/Göynük field, and named as the Kayalık Stream MSS. 113 samples were systematically collected in Kayalık Stream MSS. Among these, 28 samples belong to bituminous rocks. Pyrolysis analysis was performed for 28 bituminous samples, which contain organic material, by using Rock-Eval VI instrument in TPAO laboratories. Minimum and maximum Total Organic Content (TOC) in rocks are 0.40 wt% and 8.25 wt%, respectively (with average value of 3.76 wt%). In order to better determine the element enrichments in the basin, both bituminous and non-bituminous rocks were separately subjected to element analyses. Inorganic chemical analyses of samples, which had been pulverized in agate mortar, were carried out in Acme Analytical Laboratories Ltd. (Canada) using ICP-ES (ICP emission spectrometry) and ICP-MS (ICP mass spectrometry) techniques. By using ICP-ES method, major and trace element concentrations were calculated in 113 samples. REE analyses were performed by ICP-MS method. Again, total sulfur, total carbon and inorganic carbon analyses were carried out in ACME Analytical Laboratories Ltd. (Canada) using Leco device in 113 samples. Element abundances obtained were compared and interpreted based on rocks; besides, their geochemical behaviors were investigated calculating correlation coefficients. Enrichment values in elements in our study area were compared with other elements in worldwide known reducing environments.

3. Geologic Setting

The basement of the study area is constituted by Lower Paleozoic Bolu granitoids which outcrops in south of Göynük basin and by metamorphic rock types (Blumenthal, 1948; Saner, 1978*a*). Blumenthal (1948) stated that Bolu granitoid basically developed in pre Upper Ordovician, but there had been other intrusions into this body. These rocks are massive, medium to fine grained granites enriched in potassium feldspar.

The oldest units in vicinity of the study area are Upper Cretaceous in age. These are formed by Seben formation, which is composed of gray to greenish gray, limestone banded, marl and sandstone at the bottom, and by the conformably overlying Taraklı formation represented by shale, marl and sandstone. The Upper Cretaceous units are both laterally and vertically transitional with Paleocene-Eocene units. From bottom to top; these units are formed by Beşikkaya Formation Limestone Member (sandstone-marl member and limestone-marl member), Agsaklar Formation (conglomerate-sandstone member, marl member, limestone member), the overlying Hatıldağ Formation (productive bituminous shale member/ sterilized bituminous shale member), and by the Kabalar Formation (red marls consisting of sandstone and conglomerate lenses) at the top (Figure 1). Bituminous shales located in middle parts of the Hatıldağ Formation are brownish beige in color, and are sometimes intercalated with marl and claystone. Total thickness of bituminous shales is 290 m of which their thicknesses vary between 0.01-9 m.

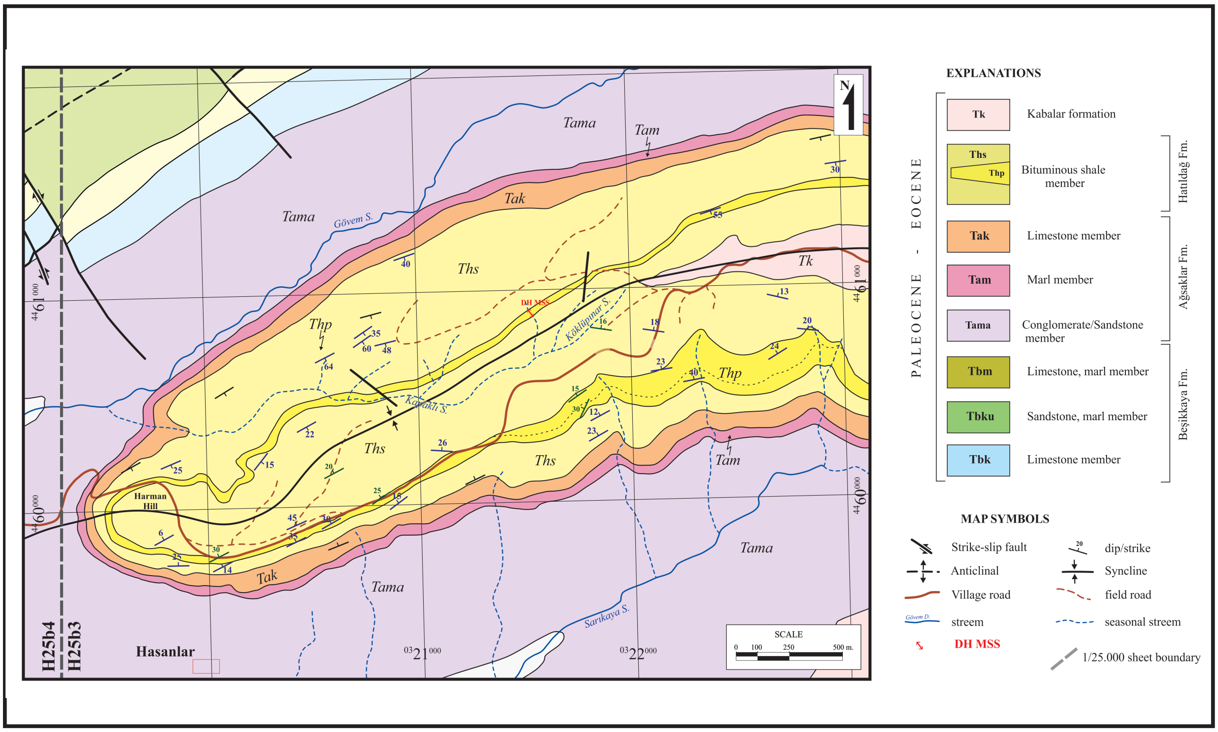

Figure 1- Geological map of the study area (Modified from Yanılmaz et al, 1980; Şengüler, 2012).

The regression of the sea which had started at the end of Upper Cretaceous from south to north also continued in Paleocene. Shallow marine limestones (Beşikkaya Formation) were deposited in Paleocene in the basin which became gradually shallow. Marine depositions have continued in a controlled way during Paleocene. Delta formations of the regressive marine and the coastal flat and coastal plain formations have controlled the rock deposition. Meandering river channel deposits, flood plain deposits and deposits with marine intercalations, which are observed in formations, indicate that the region was subjected to marine transgression in Paleocene-Eocene times. The marine transgression is distinctive by a typical sediment assemblage around Kabalar village in the study area (Saner, 1978*a*). The region also preserved its marine character in Eocene. The depth did not exceed 150-300 m in this period, and the deposition of bituminous shale, bituminous claystone and bituminous marl occurred in protected lakes behind barriers which had formed as a result of marine regression.

4. Findings and Discussion

4.1. Element Enrichments in Rocks enriched by Organic Material

Organic carbon content of bituminous rocks depends on biological productivity, prevention and sedimentation rate. Bituminous rocks are not only rich in organic material such as petroleum source rocks but also in important metals. The significant difference of metal bearing shales than petroleum sources is that they can form economic mineral deposits. Only 1%

organic carbon is enough for sulfate microorganisms to produce H_2S by breaking up the organic matter and make the environment anoxic. As a result of high amount organic matter entrance into sediment, the metal enrichments in significant amounts occur in the form of metal sulfides in periods when the groundwater is reducing/anoxic (Mao et al., 2002). Most major elements (Si, Al, Fe, K, Ca, Mg, Na, Ti, Mn and P; according to decreasing order in amount) are affected by biological processes and diagenesis. Silica is not only located in the structural lattice of clay minerals, feldspar or quartz, but also form an important component of plankton residuals such as amorphous opal. Iron is extremely sensitive in reducing environments and can participate into sediments as pyrite in the form of iron sulfide. Besides, the iron is observed as structural component on mineral grains and in the form of oxide/hydroxide layer (Canfield et al., 1992). They are located in calcium and few magnesium carbonate components. Manganese has a tendency to be reductive like iron at high Mn values of minimum oxygen water zone (Bender et al., 1977; Lewis and Luther, 2000). But it does not form stable sulfides except for special cases (Böttcher and Huckriede, 1997; Hucriede and Meischner, 1996). Trace element geochemistry of Namibia and Californian Gulf upwelling sediments have been investigated by Brongersma-Sanders et al. (1980) and Calvert and Price (1983). These investigators showed that certain trace elements such as; As, Ba, Cd, Cr, Cu, Mo, Ni, V, Zn had significantly been enriched.

Generally; metals exhibit a remarkable enrichment within laminated, organic rich facies deposited especially under euxinic conditions, and low enrichments in reverse bioturbated, organic poor facies. Based on temporal sea water data, the presence of trace element bio-accumulation in sediment composition by marine planktons and continuing regeneration processes were detected also for upwelling sediments of the Californian Gulf. As a result, the elements such as; V, U and Mo were derived from an early diagenetic source and intruded from water column into sediment by diffusion (Table 1).

Table 1- Major and Trace Element/Al Ratios on the Aged and Current Sedimentary Rocks (Brumsack, H-J., 2006).

Element	Averege Shale	Peruvian coast	Namibia mud	Gulf of California	Mediterranean sapropels	Black Sea-1	Black Sea-2	C/T Demerara rise	C/T Averege	C/T Gubbio
Si/Al	3,11	4,33	30,2	6,29	2,65	3,08	2,98	6,13	7,36	16,4
Ti/Al	0,053	0,052	0,08	0,049	0,061	0,048	0,044	0,053	0,05	0,044
Fe/Al	0,55	0,45	0,8	0,46	1,22	0,65	0,57	0,62	0,77	1,33
Mg/Al	0,18	0,28	0,38	0,2	0,39	0,3	0,28	0,24	0,22	0,23
Ca/Al	0,18	1,5	2	0,31	4,07	5,15	0,77	8,57	2,15	0,22
Na/Al	0,13	0,98	0,91	0,23	0,45	0,98	0,78	0,41	0,26	0,05
K/Al	0,34	0,28	0,39	0,29	0,25	0,3	0,3	0,26	0,28	0,37
P/Al	0,008	0,096	0,17	0,022	0,016	0,018	0,019	0,07	0,047	0,046
Ag/Al	0,008	0,12	0,148	0,042	0,12	0,079	0,076	0,73	0,73	0,78
As/Al	1,1	4,3	11	1,35	15,4	4,15	2,87	8,6	7,9	18
Ba/Al	66	69	298	121	341	174	260	155	204	3638
Bi/Al	0,015	0,045	0,08	0,03	0,044	0,07	0,06	0,042	0,065	0,39
Cd/Al	0,015	8,5	26	0,55	2,7	0,26	0,27	5,81	6,27	2,14
Co/Al	2,1	1,2	2,9	1,4	17,4	6,2	3,8	2,81	14,7	5,9
Cr/Al	10,2	24,4	72	9,4	28,3	12,2	12,8	57	41,4	33,9
Cu/Al	5,1	11,6	32	5,8	33,1	17,6	23,7	31,9	43,8	63
Mn/Al	96	52	28	41	202	129	56	42	125	23
Mo/Al	0,15	10,6	37	2,6	27,9	14,7	26,2	37,7	61,4	12,8
Ni/Al	7,7	20,2	41	8,1	54,6	16,7	24,5	60	65,2	52,4
Pb/Al	2,5	3,5	3,7	3,6	2,9	5,3	3,7	3	4,5	4
Rb/Al	16	12,3	22	15	12,1	15,6	15,7	11,2	18,1	16,7

Table 1- (continued)

Re/Al	0,11	1,12	2,25	n.d.	7,55	0,98	1,22	3,1	4,9	2,85
Sb/Al	0,17	0,5	n.d.	0,85	2,67	0,57	0,33	4,38	4	1,56
Sr/Al	34	86	181	35	200	271	59	318	106	122
Tl/Al	0,077	0,33	2,5	0,08	0,58	0,12	0,18	1,19	1,2	3,44
U/Al	0,42	2,3	28,6	1,21	4,1	3,2	3,3	4,87	6,4	2,9
V/Al	15	38	126	21,5	139	29	44	491	271	271
Zn/Al	11	24	29	18,7	25	19	18	246	459	249
Zr/Al	18	21	25,2	n.d.	24	18	15	15	18	19

4.2. Major Element Enrichments

In correlation studies of major oxides made by Al_2O_3, Al_2O_3 element gave very high positive correlation with SiO_2, Fe_2O_3, Na_2O and K_2O elements, indicating that all these elements were detritic and derived from the same source. However; Al_2O_3 gave a very high negative correlations with MgO and CaO indicating that these elements were derived from different origins, and the sources of MgO and CaO elements were carbonate in origin (Table 2).

Table 2- Correlation of major oxides of the study area.

Kayalık Stream MSS	**Corg**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**MnO**
Corg	1,00	-0,16	-0,15	-0,25	0,10	-0,13	-0,14	-0,03	-0,16	0,07	-0,38
SiO_2		1,00	0,82	0,81	-0,50	-0,74	0,22	0,71	0,75	-0,09	0,06
Al_2O_3			1,00	0,93	-0,74	-0,44	0,67	0,56	0,97	0,05	0,27
Fe_2O_3				1,00	-0,78	-0,35	0,63	0,52	0,92	0,04	0,48
MgO					1,00	-0,13	-0,76	-0,21	-0,74	-0,41	-0,53
CaO						1,00	0,25	-0,69	-0,35	0,39	0,43
Na_2O							1,00	-0,15	0,72	0,25	0,55
K_2O								1,00	0,50	-0,19	-0,16
TiO_2									1,00	0,06	0,35
P_2O_5										1,00	0,11
MnO											1,00

The increase in Si/Al ratio expresses an increase in detritic quartz amount; however, the decrease in this amount could express an increase in clay amount. The increase in K/Al ratio presents more micaeous clay input and probably a fine grained K-feldspar increase. But, there was not observed any remarkable enrichment in K, among samples of the study area; on the contrary, there was observed some depletion in some samples. It indicates that, illite type clay in samples is niether much available, nor is the depositional environment a deep marine. In Kayalık Stream MSS samples, the enrichment of major elements with respect to Al normalized shales are in question; even, there is observed an enrichment more than 100 times in Ca and Mg elements (Figure 2). It shows that our sedimentary environment is in a system which is suitable for carbonate deposition. Similarly; high enrichments observed in Mn again originate from carbonate minerals. When major element enrichments of bituminous samples in Kayalık Stream MSS were totally studied, there were observed enrichments in Si, Mn, Cr elements ranging between 1 to 10 times. However; the enrichment amounts in Fe, Na, K and Ti elements range between 1 to 5 times, and there is depletion in P element. The remarkable point here is the enrichments up to 100 times in Ca and Mg elements. This shows that the sedimentary environment in Hatıldağ field is generally carbonated (suitable to limestone and dolomite deposition) (Figure 2). Low Si concentrations indicate that detritic silica input is extremely low in depositional environment, and the depositional environment of bituminous rock is a water column which is generally calm and stagnant.

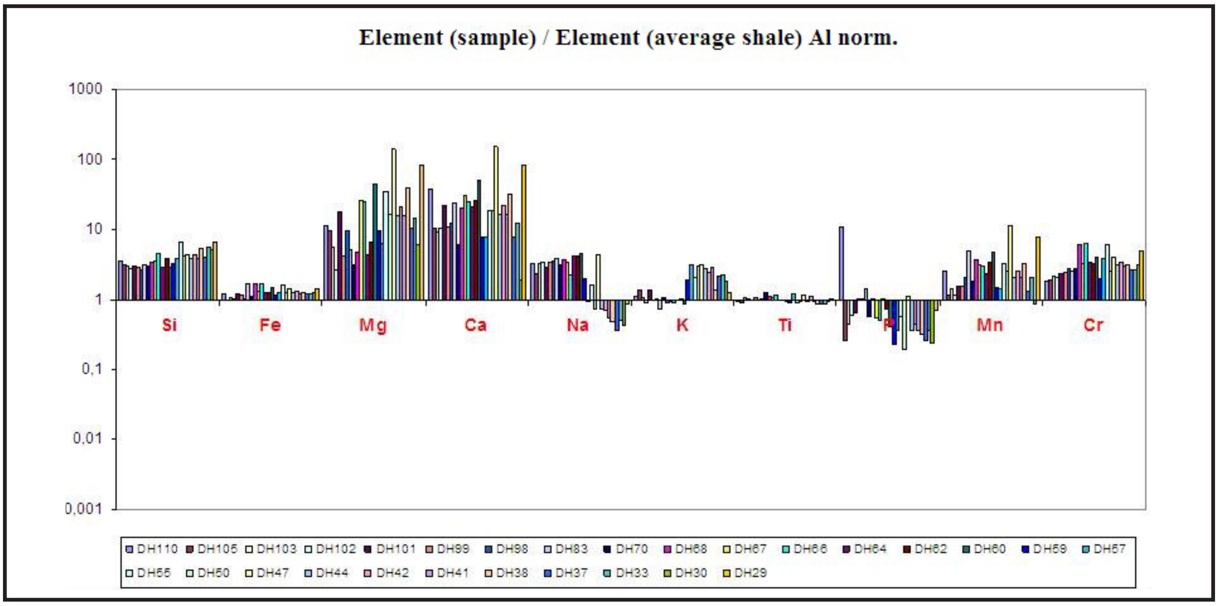

Figure 2- Enrichment of Kayalıkdere samples compared to the major elements shales which were normalized by Al.

4.3. Trace Element Enrichments

The chemical composition of the main rock is importantly affected from local or regional soil and water chemistry. Therefore; the atmospheric water in sedimentation becomes effective in element enrichment. Elements may be deposited in much sulfurous reducing depositional environments by being absorbed or as sulfides (FeS_2, PbS, CuS, CoS, ZnS, MoS_2). For this reason; some trace metals become enriched in organic rich rocks. Enrichment Factors (EF) are determined by normalizing clastic input of each trace element by Al and comparing these ratios with normal shale. This approach is used by many authors in assessing the trace element enrichments in accumulated sediments today and in the past (Calvert and Pedersen, 1993). EF is calculated as; $EF_{element}X=X/Al_{sample}$ / $X/Al_{average\ shale}$. If EF_X is greater than 1, then $X_{element}$ is enriched with respect to average shale, if it is less than 1, then it is depleted.

All trace elements (TE) are affected by stronger processes under low oxygen conditions like; the intense increase of organic carbon amount as it was in Mn/Fe redox cycle in the presence of H_2S within water column in sedimentary redox boundary or under euxinic conditions (Pratt and Davis, 1992; Calvert and Pedersen, 1993; Morse and Luther, 1999). The obtained results which are related with the characteristic trace element samples and redox environments are as follows; (1) while upwelling sediments generally become enriched in Cd and P, they become depleted in Co and Mn, (2) sapropels reflect strong sulfidization in anoxic water column and have a tendency of high enrichment in Ba, Mo, S, Re, As, Cu, Ni, Sb, and Fe, (3) upwelling systems, the distance of H_2S accumulation into sediment sea water interface, bio-accumulation intensity and its reproduction reflect the broad area of environmental conditions which play an important role for trace element accumulation, (4) the trace element content of anoxic basins is controlled by being based on the trace element presence in water column and sedimentation rate, (5) very high bio-production is the main key which transforms oxic environment into anoxic environment (Brumsack, 2006). One of the most significant discoveries related with trace element behaviors in oceans is that these elements occur within processes of biologic cycle (Bruland, 1983). Pleistocene sapropels consist of Co, Cu, Cr, Ni, and V metals, and Cd, Mo, Re, Sb, Tl and U metals in fewer amounts, and Bi element in much fewer amount (Brumsack 1989; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993). These elements are deposited either as sulfides (especially iron sulfides) or as connected to an organic matter (Calvert et al., 1985; Jacobs et al., 1985). Some metals (Mo, U, V) may accumulate into the sediment by diffusion or after reduction during early diagenesis (Brumsack and Gieskes, 1983; Shaw et al., 1990).

In samples belonging to the study area, the enrichments of Ni, Sc, Ba, Be, Co, Cs, Hf, Sn, Sr, U, Th, Ta, V, W, Cu, Pb, As, Sb, Ag and Se elements mainly show an increase compared to average shale. In addition; Ni, Sr, W, As, Ag and Se elements become enriched 100 times more than average shale in some samples (Figure 3). Some elements such as; Ni, Co, U, V, Pb, Cu elements to show very high enrichment probably depends on the presence of C_{org}. High Ag enrichments might be due to the retention in silicate bio-geochemical cycle, the particles in groundwater or due to the adsorption in sulfide and diagenetic Selenides (Ndung'u et al., 2001; McKay and Pedersen, 2002; Crusius and Thomson, 2003).

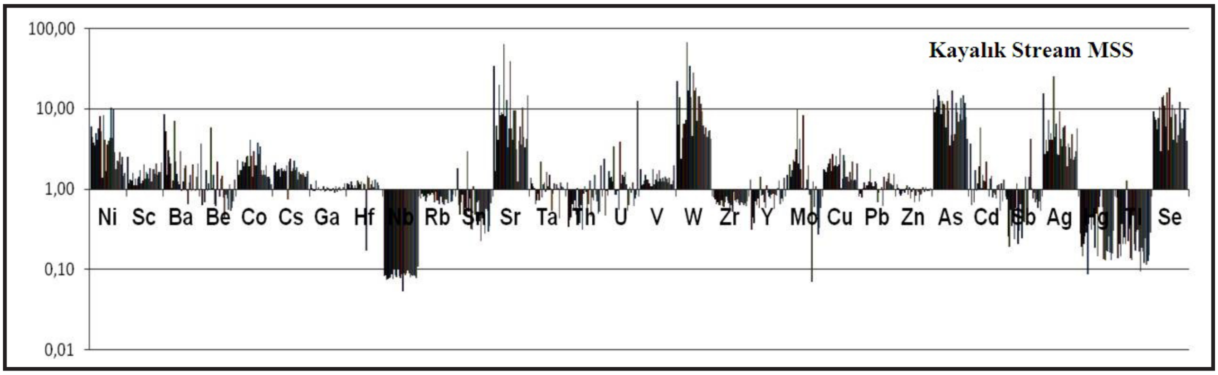

Figure 3- Enrichment of Kayalıkdere samples trace elements compared to the normalized shale which were normalized by Al.

4.4. The Comparison of Element Enrichments with Reducing Environments in the World

The enrichment values of major and trace elements of the Kayalık Stream MSS were compared with element enrichments of Peru Coastal Shelf Sediments, Namibia (Africa) Coastal Shelf Sediments, Mediterranean Sapropels, Black Sea Sapropels, Cenomanian/Turonian Demerara Rise Sediments and Cenomanian/Turonian Gubbio Sediments (Table 3, Figure 4). Considering average enrichments, it was seen that there were enrichments in different element accumulations of the regions, which had been deposited in organic matter rich, anoxic/euxinic environments. These differences are related with the variability of redox conditions of depositional environments. For instance; as the organic matter accumulation will be low or absent in oxic conditions, the conditions (organic matter or sulfides) in which metals would be accumulated will not develop. Elements in semi-sulfidic environments are deposited in the form of organic ligands by being attached to organic structures. Elements in sulfidic environments prefer being deposited in the form of sulfides (FeS_2, PbS, CuS, MoS_2 etc.). Especially; bituminous samples in the study area to display element enrichments in wide range indicates non-homogeneity of the depositional environment of Hatıldağ field and the frequent variation of redox environmental conditions. Elements like; Mo and Co, which generally show enrichment with organic carbon, in Hatıldağ field samples, are quite lower than enrichment rates of sediments in other regions. This indicates that, the depositional environment in Hatıldağ field is less sulfidic/anoxic compared to other environments.

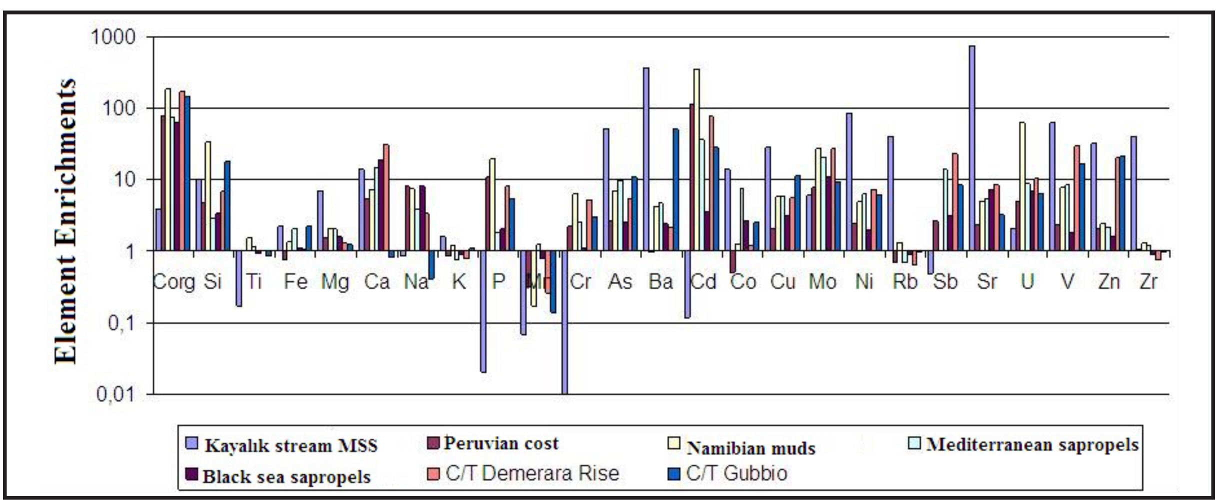

Figure 4- In Kayalıkdere major and trace element enrichment's averages in comparison with other reducing conditions of the world.

Table 3- Major and trace element enrichments of Peruvian Coast, Namibia muds, Mediterranean and Black Sea sapropels, C/T Demerara Rise and C/T Gubbio organic rich rocks of the studied samples.

Major Element	**Kayalık Stream MMS**	**Peruvian Coast**	**Namibian Muds**	**Mediterranean sapropels**	**Black Sea sapropels**	**C/T Demerara Rise**	**C/T Gubbio**
C_{org}	3,76	76,96	185,22	73,91	63,91	175,22	147,39
Si	10,1	4,75	33,10	2,90	3,38	6,72	17,97
Ti	0,17	0,98	1,51	1,15	0,91	1	0,83
Fe	2,2	0,76	1,36	2,07	1,10	1,05	2,25
Mg	6,98	1,49	2,03	2,08	1,6	1,28	1,23
Ca	13,84	5,43	7,24	14,73	18,64	31,02	0,80
Na	0,85	8,17	7,58	3,75	8,17	3,42	0,42
K	1,56	0,84	1,17	0,75	0,90	0,78	1,11
P	0,02	10,97	19,43	1,83	2,06	8	5,26
Mn	0,07	0,32	0,17	1,24	0,79	0,26	0,14
Cr	0,01	2,17	6,4	2,52	1,08	5,07	3,01
Trace Element	**Kayalık Stream MMS**	**Peruvian Coast**	**Namibian Muds**	**Mediterranean sapropels**	**Black Sea sapropels**	**C/T Demerara Rise**	**C/T Gubbio**
As	51	2,65	6,77	9,48	2,55	5,29	11,08
Ba	370	0,95	4,11	4,70	2,4	2,14	50,18
Cd	0,12	113,33	346,67	36	3,47	77,47	28,53
Co	14	0,51	1,22	7,33	2,61	1,18	2,48
Cu	29	2,06	5,69	5,88	3,13	5,67	11,2
Mo	6	7,71	26,91	20,29	10,69	27,42	9,31
Ni	85	2,38	4,82	6,42	1,96	7,06	6,16
Rb	40	0,70	1,26	0,69	0,89	0,64	0,95
Sb	0,5	2,67	n.d.	14,24	3,04	23,36	8,32
Sr	755	2,29	4,83	5,33	7,23	8,48	3,25
U	2	4,97	61,84	8,86	6,92	10,53	6,27
V	64	2,34	7,75	8,55	1,78	30,22	16,68
Zn	32	2,02	2,44	2,11	1,6	20,72	20,97
Zr	40	1,05	1,26	1,2	0,9	0,75	0,95

Major and trace elements in samples of the study area, normalized by Al, were compared with elements deposited under other anoxic/euxinic conditions in the world. Thus, there were observed enrichments generally in the concentration of Ca, Mg, K, Cr, Sr and Ba elements in Kayalık Stream MSS. Especially; the concentrations of Ca, Ba and Mg elements were estimated quite high (Figures 4 and 5, Table 4). This indicates that, redox conditions of the depositional environment in Hatıldağ field is generally subjected to oxic/dioxic conditions. The basin is quite carbonated and its redox condition is less sulfidic compared to other environments. The high carbonate and dolomite contents in studied bituminous samples also support this fact.

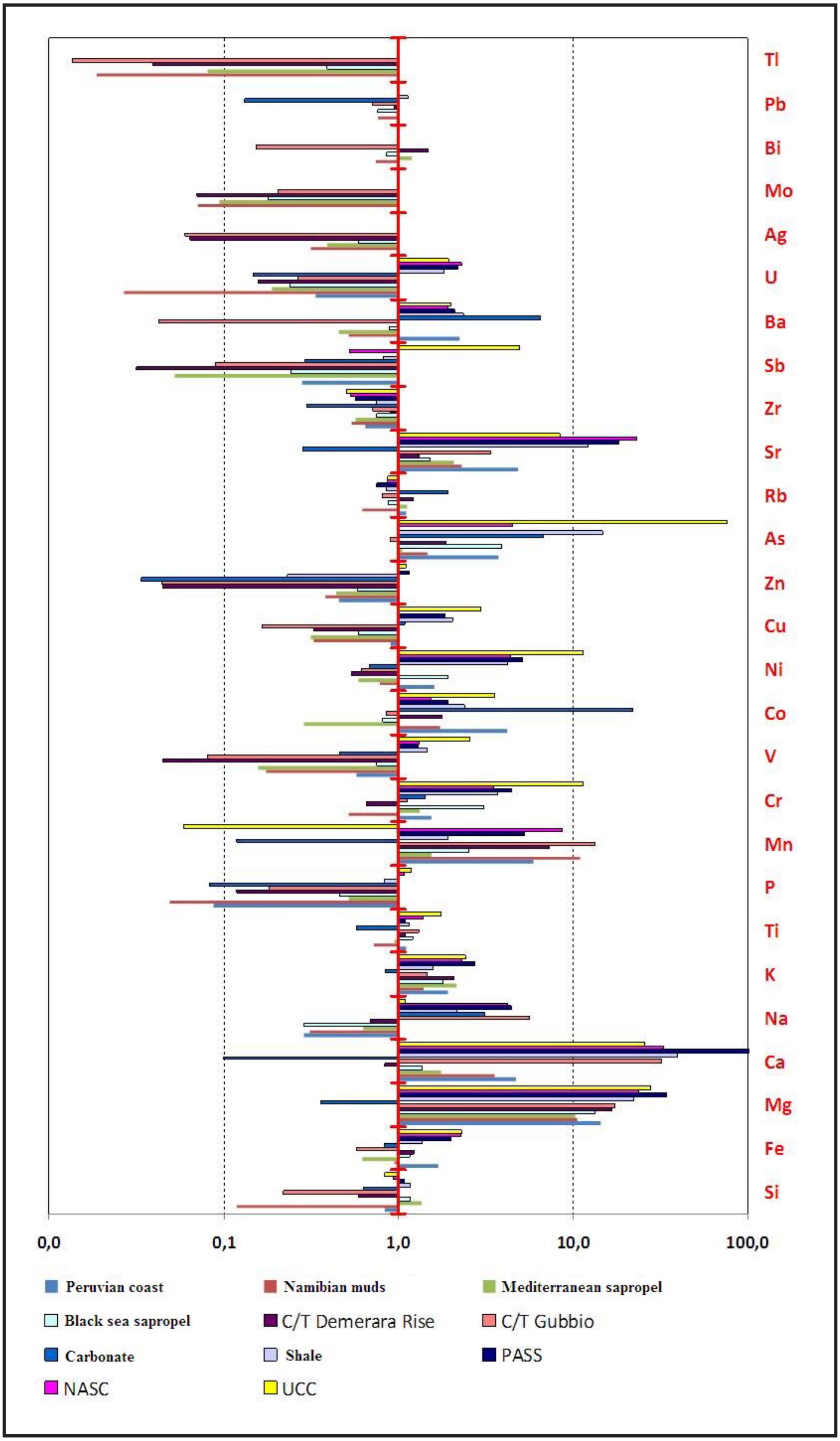

Figure 5-Kayalıkdere’s bituminous samples enrichments based on Peruvian Coast, Namiby Mud, Mediterranean Sapropel, Black Sea Sapropel, the C/T Demerara Rise, C/T Gubbio, carbonate, shale, PASS, NASCAR and UCC enriched samples.

Table 4- Average enrichment values of elements in Kayalık Stream MSS with respect to other elements in reducing environment in the world.

	Elem./ Al	[Element (DH)/Al] / [Element (Other reducing environments)/Al]										
El.	**DH ÖSK**	**Peru Coast**	**Namibian mud.**	**Mediterranean sapropels**	**Black Sea sapropels**	**C/T Demera. Rise**	**C/T Gubbio**	**Carbonate**	**Shale**	**PASS**	**NASC**	**UCC**
Si	3,61	0,83	0,12	1,36	1,17	0,59	0,22	0,63	1,16	1,09	0,94	0,83
Fe	0,76	1,69	0,95	0,62	1,17	1,23	0,57	0,84	1,39	1,99	2,28	2,32
Mg	4,03	14,38	10,60	10,32	13,42	16,78	17,50	0,36	22,37	34,59	23,79	27,81
Ca	7,12	4,75	3,56	1,75	1,38	0,83	32,39	0,10	39,58	103,67	33,17	25,79
Na	0,28	0,29	0,31	0,63	0,29	0,69	5,65	3,14	2,17	4,45	4,19	1,10
K	0,54	1,93	1,39	2,16	1,80	2,08	1,46	0,85	1,59	2,76	2,30	2,42
Ti	0,06	1,11	0,72	0,95	1,21	1,09	1,32	0,58	1,16	1,09	1,40	1,76
P	0,01	0,09	0,05	0,52	0,46	0,12	0,18	0,08	0,83	0,99	1,09	1,18
Mn	0,03	5,92	11,00	1,54	2,57	7,33	13,39	0,12	1,92	5,29	8,69	0,06
Cr	0,00	1,55	0,52	1,33	3,10	0,65	1,13	1,43	3,72	4,44	3,50	11,50
V	21,91	0,58	0,17	0,16	0,76	0,04	0,08	0,46	1,46	1,29	1,33	2,59
Co	5,04	4,20	1,74	0,29	0,81	1,79	0,85	21,90	2,40	1,93	1,55	3,58
Ni	32,30	1,60	0,79	0,59	1,93	0,54	0,62	0,68	4,19	5,19	4,40	11,47
Cu	10,45	0,90	0,33	0,32	0,59	0,33	0,17	1,10	2,05	1,85	n.a.	2,97
Zn	11,03	0,46	0,38	0,44	0,58	0,04	0,04	0,03	0,23	1,15	n.a.	1,10
As	16,18	3,76	1,47	1,05	3,90	1,88	0,90	6,80	14,71	n.a.	4,50	76,63
Rb	13,66	1,11	0,62	1,13	0,88	1,22	0,82	1,91	0,85	0,75	0,86	0,87
Sr	414,11	4,82	2,29	2,07	1,53	1,30	3,39	0,29	12,18	18,29	23,04	8,41
Zr	2,66	0,65	0,54	0,57	0,75	0,91	0,72	0,30	0,75	0,57	0,54	0,51
Sb	13,59	0,28	n.a.	0,05	0,24	0,03	0,09	0,29	0,82	n.a.	0,53	4,96
Ba	155,14	2,25	0,52	0,45	0,89	1,00	0,04	6,52	2,35	2,11	1,93	2,00
U	0,77	0,34	0,03	0,19	0,24	0,16	0,27	0,15	1,84	2,20	2,29	1,96
Ag	0,05	n.a.	0,32	0,39	0,59	0,06	0,06	n.a.	n.a.	n.a.	n.a.	n.a.
Mo	2,64	n.a.	0,07	0,09	0,18	0,07	0,21	n.a.	n.a.	n.a.	n.a.	n.a.
Bi	0,06	n.a.	0,75	1,20	0,85	1,50	0,15	n.a.	n.a.	n.a.	n.a.	n.a.
Pb	2,84	n.a.	0,77	0,98	0,77	0,95	0,71	0,13	1,14	n.a.	n.a.	n.a.
Tl	0,05	n.a.	0,02	0,08	0,39	0,04	0,01	n.a.	n.a.	n.a.	n.a.	n.a.

5. Results

As a result of correlation studies of major oxides made by Al_2O_3, quite high positive correlations were obtained in SiO_2, Fe_2O_3, Na_2O and K_2O elements. This indicates that, all these elements are continental and derived from the same origin. Al_2O_3 to give quite high negative correlations with MgO and CaO shows that these elements are carbonate in origin.

The enrichments of Ni, Sc, Ba, Be, Co, Cs, Hf, Sn, Sr, U, Th, Ta, V, W, Cu, Pb, As, Sb, Ag, and Se elements among trace elements mostly show an increase with respect to average shale in bituminous samples of the Kayalık Stream MSS.

Enrichments in Ca and Mg elements in bituminous samples of the Kayalık Stream MSS are nearly 100 times. While there are observed variations in enrichments between 1 to 10 times in Si, Mn and Cr elements, the enrichment values in Fe, Na, K and Ti elements vary between 1 to 5 times. However, there was observed depletion in P element.

Element enrichments of the Kayalık Stream MSS were normalized by Al and compared with Peruvian Coast, Namibia muds, Mediterranean sapropels, Black Sea sapropels, C/T Demerara Rise, C/T Gubbio, Carbonate average, Average Shale, PASS, NASC and with UCC rocks. As a result, enrichments generally in Mg, Ca, K, Cr, Sr and Ba concentrations were observed. It indicates that, the depositional environment in Hatıldağ Field is quite carbonated and its redox conditions are less sulfidic with respect to other anoxic/euxinic basin conditions. The high carbonate and dolomite contents in studied samples also support this fact.

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