

AN APPROACH TO PROVENANCE, TECTONIC AND REDOX CONDITIONS OF JURASSIC-CRETACEOUS AKKUYU FORMATION, CENTRAL TAURIDS, TURKEY

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ABSTRACT.- Late Jurassic-Early Cretaceous Akkuyu formation was deposited in a marine carbonate platform in Central Taurids. The organic material of the unit is composed of Type III kerogen which is woody material transported from the land. Late Jurassic- Early Cretaceous is an important period which great anoxic events in deep sea bottom occurred due to the primary organic productivity in global sea surface. Use of several trace elements values (Ni, V, U, Cr, Co, Th) revealed that Late Jurassic-Early Cretaceous Akkuyu formation shows oxic, disoxic and anoxic paleoredox conditions. In this period the primary productivity was considerably high. Examination of specimen derived from Akkuyu formation revealed that there exist a very good positive relationship between the major oxides of Al_2O_3 , SiO_2 , Fe_2O_3 , TiO_2 , and K_2O . These combinations of major oxides indicate a detrital origin of source rock. Chemical weathering evaluations of Central Taurids in Jurassic-Cretaceous period indicated moderate and strong weathering of source rock. K_2O/Na_2O versus SiO_2 ; SiO_2/Al_2O_3 versus K_2O/Na_2O ; Al_2O_3/SiO_2 versus $Fe_2O_3 + MgO$ ve TiO_2 versus $Fe_2O_3 + MgO$ diagrams indicated that Akkuyu formation was deposited along active and/or passive continental margin and derived from basalt and basalt+granite mixed rocks.

Key words: Late Jurassic-Early Cretaceous, Provenance, Central Taurids, Redox, Major oxide

INTRODUCTION

The study area is located 100 km NE of the city of Antalya (Figure 1). The late Jurassic-early Cretaceous Akkuyu formation was deposited in a marine carbonate platform in the Central Taurids. This carbonate platform was faulted and separated into several tectonic slices due to intense tectonic activity. In the late Jurassic-early Cretaceous period, as a result of global warming, ice sheets were melted, large-scale marine transgressions took place and anoxic events occurred at the sea bottom because of high primary organic productivity in the shelf areas depending on high oxygen, dissolved phosphate and nitrate abundance (Pedersen and Calvert, 1990; Caplan and Bustin, 1998).

The Akkuyu formation is within the Geyikdađı Unit of autochthon or parautochthon character and the basement of unit is comprised by gray colored, thin-medium bedded clayey limestones which change to clayey thin bedded limestones to the top. In addition, the unit is black colored, bituminous, foliated and contains shale interlayers (Figure 2).

There are some geological and petroleum geology studies conducted in the Central Taurids region and its vicinity (Blumenthal, 1951; Martin, 1969; Monod, 1977; Toker et al., 1993; Sonel et al., 1995; Albayrak, 1995; Sari et al., 2008; Koca et al., 2010). In shelf areas, particularly dissolved phosphate, nitrate salts and big amount of oxygen content cause to organic productivity to be

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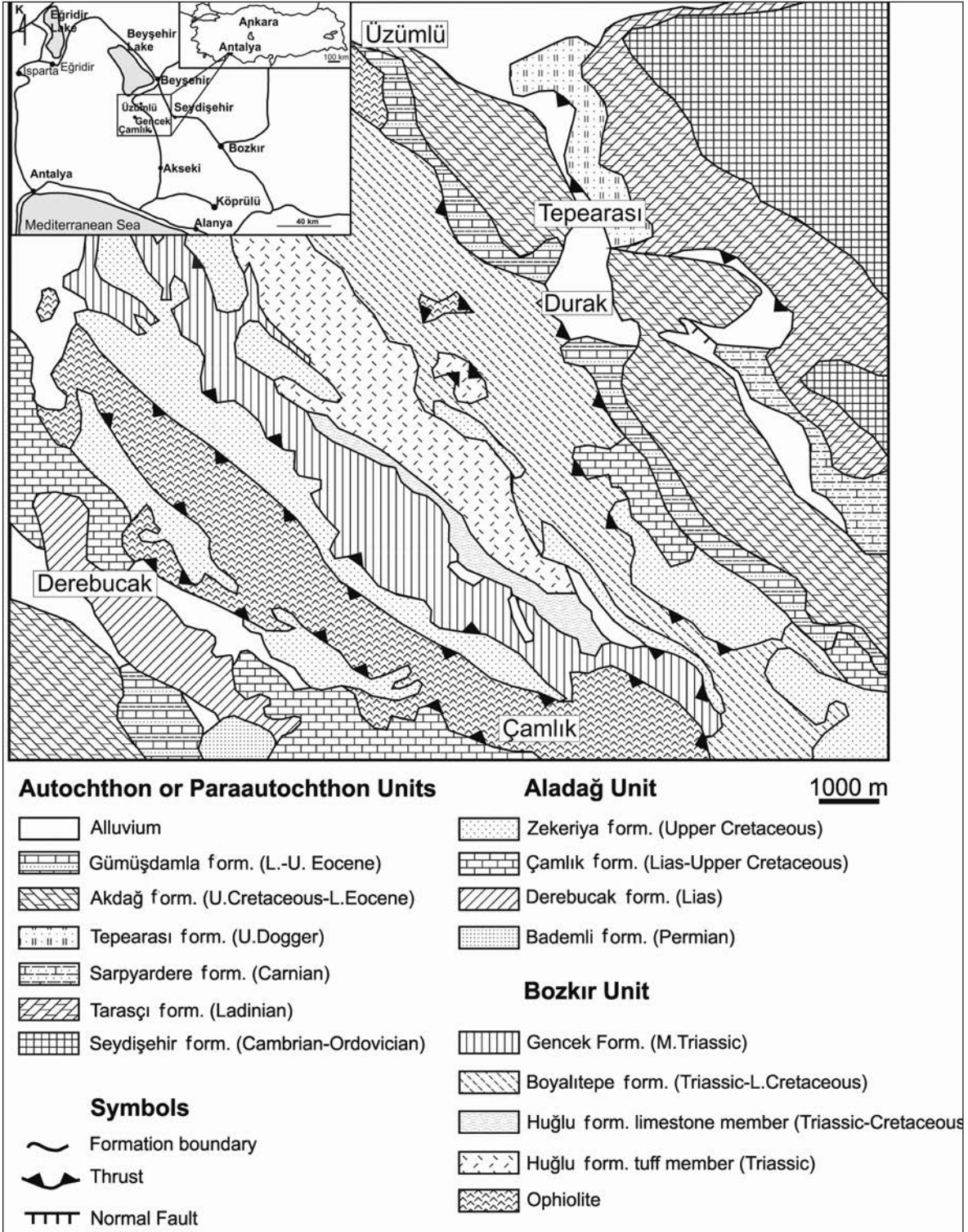


Figure 1- Geology map of the study area (Sarı et al., 1997)

high. As a result of high organic productivity in the photic zone, upper water column cannot meet the oxygen demand of organisms in time and therefore, plant and animal planktons die in massive amounts and accumulate at the sea bottom. Because of oxygen deficiency and H_2S abundance and the organic accumulation at the bottom, bottom water changed its character to anoxic/euxinic in time which facilitated organic material enrichment like exemplified in the Akkuyu formation of Central Taurides.

Organic material-rich rocks are not only important oil and gas sources but they also host economically essential elements and therefore comprise potential mineral deposits. There are a number of mineral deposits which are economically exploited from the organic material-rich rocks. For example, uranium is extracted from bituminous shales in Sweden (Andersson et al., 1985).

The main metal deposits in shale-like rocks were formed in Phanerozoic in Australia, North America and Africa. The most important and best known deposits in Africa are Zambia copper belts where a series of stratiform copper (Cu)-cobalt (Co) depositions occur in a 120 km² belt (Fleischer et al., 1976). The first mineralization contains at least 30×10^6 metric tons of metallic copper (or 3% copper and 0.1-0.3% cobalt in 10^9 metric tons of deposit). Fleischer et al. (1976) described different types of Zambian copper-bearing shale deposits.

In some large, best known shale bed rocks such as Proterozoic aged Mt. Isa, Hilton, McArthur River and Lady Loretta in Australia, Pb-Zn-Ag were deposited (Gustavson and Williams, 1981). In North America best known shale-associated mineral deposits include Proterozoic White Pine Cu mineralization in Michigan and Sullivan Pb-Zn deposits in British Columbia. White Pine Cu mineralization occurs in Proterozoic Nonesuch shale which is thought to be lacustrine deposits in the Keweenaw Rift

(Gustavson and Williams, 1981).

As the organic material content of rocks increases U, Ba, Sb, Cd, Mo, Rb, Se, As, Zn, Cu, Ni, Co, Cr and V element concentrations also increase. The reason for significant enrichment of these elements in organic material-rich rocks rather than country rocks is attributed to primary production of organic material in upper water, column sedimentation rate, redox conditions (Eh, pH) of depositional environment, H_2S enrichment by sulfate-reducing bacteria, organic material preservation and precipitation of sulfide components.

In this study, depositional conditions of organic material-rich rocks of Akkuyu formation are determined based on their organic material contents. The source and weathering levels of samples are also investigated.

MATERIAL AND METHOD

In this study, a number of 10 organic material-rich rock samples systematically collected from late Jurassic-late Cretaceous Akkuyu formation (Central Taurids) were subjected to various geochemical, petrographic and clay analyses. The organic carbon analysis (TOC %) was performed at TPAO laboratories using WR - 12 type carbon analysis device. Using the pyrolysis device (Oil Show Analyzer) S_1 , S_2 , S_3 , T_{max} , oxygen index (OI) and hydrogen index (HI) values were determined. From HI and T_{max} values kerogen types were identified. Major oxide (Al_2O_3 , SiO_2 , MgO, CaO, K_2O and TiO_2) and trace element (U, Ba, Cu, Ni, Cr, As, V, Zn, Sb, Co, Mo and Cd) analyses of organic carbon-rich (C_{org}) samples of the Akkuyu formation were carried out at Engineering Faculty Geochemistry Laboratories of the Ankara University. Samples were first prepared for geochemical analysis at the Micro Analysis-ICP Laboratory. Samples were grinded on a Retsch brand automatic rock grinder and then crushed with a FRITSCH brand automatic crusher on a

carbide mill. 4 g sample was mixed with 0.9 g binding material (Wachs) and compressed under hydraulic press to have powder-pellets (with pellet diameter of 32 mm). The samples were analyzed at X-Lab 2000 model PED-XRF (Polarized Energy Dispersive XRF) device for major oxides and trace element contents. XRF analysis was conducted with Tq-7220 method. Whole rock clay analysis was carried out with Rigaku brand XRD device at MTA laboratories. The Pearson correlations were computed with the Statistica program.

Organic material type and element relations

Using the hydrogen index (HI: mgHC/g rock; $S_2 \cdot 100/TOC$) and T_{max} (°C) values from pyrolysis analysis, with the exception of sample AK-8 (Type-II), the organic material type of analyzed samples was found as Type-III (Figure 3). Type II kerogens are composed of spore, pollen, terrestrial plant cuticles, lipids, resins and marine algae whilst Type-III kerogens are made up of terrestrial plants, trees and cellulose. Deposition of organic material-rich marine sediments depends on several factors which include anoxic/low oxygenated bottom water (Erbache-ret et al., 2001), high primary productivity facilitating organic carbon flux to the sea bottom (Pedersen and Calvert, 1990; Ibach, 1982), sedimentation rate (Pedersen and Calvert, 1990), fast burial preventing microbially-mediated organic material decomposition, upwelling (Suess et al., 1987), protective adsorption of organic materials on clay minerals (Hedges and Keil, 1995) and dilution by inorganic components (Demaison and Moore, 1980).

Under anoxic conditions accumulation and transfer ratios of certain trace elements could be high and noteworthy trace element exchange also takes place in seawater (Nijenhuis et al., 1999; Morford et al., 2001). In addition, under low oxygenated conditions, organic material-rich sediments are generally enriched in redox-sensitive and sulfide-forming metals which trap

trace elements (Arnaboldi and Meyers, 2003; Brumsack, 2006). In this respect, the enrichment level of elements in organic material-rich rocks of the Akkuyu formation was investigated. Enrichments of some trace elements such as V, Co, Ni, Cu, Zn, Se, Cd, Mo, U are found to be greater than that of average shale.

Identification of Paleoredox conditions for Late Jurassic-Early Cretaceous Period

Under dioxic-anoxic and euxinic redox conditions, metals are mostly accumulated as metal sulfides. The greatest metal enrichment occurs under euxinic redox conditions which reflect complete sulfide phase (Warning and Brumsack, 2000; Arnaboldi and Meyers, 2003; Brumsack, 2006). Several trace elements such as Mo, Mn, Ni, V, U, Cr, Co have been used to evaluate paleoredox conditions (Hatch and Leventhal, 1992; Jones and Manning, 1994; Algeo and Maynard, 2004; Rimmer et al., 2004). Certain elements, which are sensitive to redox changes in marine environment and pore waters, are used for reconstruction of redox conditions in young and old sedimentary basins associated with organic material deposits and sulfide occurrences in oxygen-poor mediums (Brumsack, 2006; Tribouillard et al., 2006). Oxidation of sulfides produces a sulfate source for sulfate-reducing bacteria which facilitates anoxic conditions (Brüchert et al., 2003). It is believed that Ni and V are preferentially retained in tetrapyrrole structure which is preserved under anoxic conditions (Lewan and Maynard, 1982). Lewan (1984) suggested that V/Ni ratio in crude oil which is not altered by diagenesis reflects environmental conditions during the deposition and showed that $V/(V+Ni)$ ratio for organics forming under euxinic conditions is greater than 0.5. According to Hatch and Leventhal (1992), $V/(V+Ni)$ ratios are greater than 0.84 for euxinic conditions and in the range of 0.54 – 0.82 for anoxic conditions and between 0.46 and 0.60 for dioxic conditions. Vanadium which is incorporated into tetrapyrrole

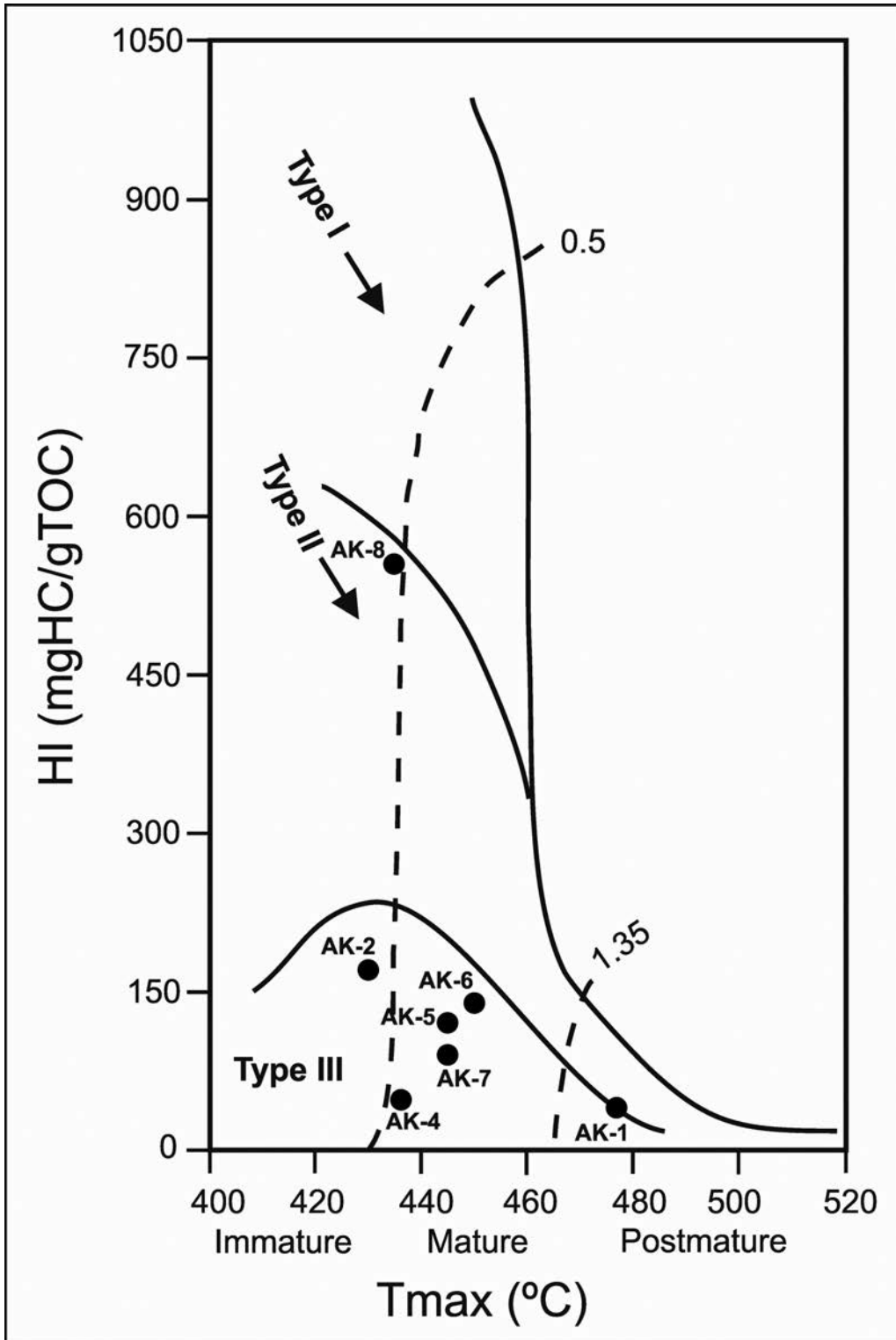


Figure 3- Kerojen Types of Akkuyu formation's samples according to HI-T_{max} graphic

structure under anoxic conditions may also be precipitated by adsorbing onto surface of clay minerals which most probably occurs after burial (Breit and Wanty, 1991). Cr is thought to be related only to detrital fraction (Dill, 1986) and it is not affected by redox conditions, and thus, high V/Cr ratios (> 4.25) are believed to reflect anoxic conditions (Jones and Manning, 1994). Jones and Manning (1994) used V/Cr ratio to evaluate the paleoenvironment characteristics. V/Cr ratio is suggested as an index for paleo-oxidation conditions (Dill et al., 1988). In reduced sediments Ni and V are retained by organic material (Lewan and Maynard, 1982). Cr and Co contents are thought to have a detrital origin (Ross and Bustin, 2006). Both Ni and Co are incorporated into pyrite structure. However, high Ni/Co ratios are believed to be related to anoxic conditions (Jones and Manning, 1994). Ni/Co value of samples of the Akkuyu formation reflects dioxic/anoxic; V/Cr ratio reflects oxic-dioxic and anoxic, V/V+Ni values reflect oxic and anoxic and U/Th ratio reflects dioxic and anoxic conditions (Figure 4; table 1).

As shown from figure 4, the basement of depositional environment of the Akkuyu formation was well oxygenated and organic productivity was abundant at surface conditions, but later, as a result of oxygen and nutrient deficiency in the upper water column, organisms (plankton and algae) were undergone a mass die off and H₂S-rich fluids issued at the bottom. In the middle levels dioxic conditions were prevailed due to insufficient H₂S whilst because of significant H₂S abundance to the upper levels anoxic conditions were dominant.

Paleoproductivity in the Late Jurassic-Early Cretaceous Period

Nutrient need of marine organisms, particularly planktonics, are met by phosphate and nitrate salts which are dissolved and transported by the rivers. Nitrogen (N) and phosphorus (P) exert a major control on biologic productivity in the marine environment (Holland, 1978). Changes in P concentration are attributed to variations in continental weathering (Algeo et al., 1995; Algeo and Scheckler, 1998), C/P variation in sedimentary organic material composition (Ruttenberg and Goñi, 1997) or variation in P flux under anoxic or very low oxygenated bottom water conditions (Ingall and Jahnke, 1997; Murphy et al., 2000). In general, Ba, P and Cd are used as geochemical indicators for paleoproductivity (van Capellen and Ingall, 1994; Filippelli et al., 1994). High P and Ba contents reflect strong primary organic productivity. The presence of P-bearing apatite which can concentrate Cd and rarely seen high Cd content can be attributed to reducing conditions prevailed at the bottom. Similarities of hydroxyapatite and frequently repeated Cd enrichment in phosphorite deposits are reported in various studies (Middleburg and Comans, 1991). In the studied samples, P and Cd concentrations are extremely enriched with respect to average shale while Ba shows slight enrichments (Figure 5). The similar Cd, P and Ba element enrichments are indicative of high productivity of environment.

The strong positive correlation between Cd/Al and P/Al pairs in the studies samples of

Table 1- Paleoredox proxies metals

	Oxic	Dysoxic	Anoxic	Euxinic
Ni/Co ¹	< 5	5 – 7	> 7	
V/Cr ²	< 2	2 – 4.5	>4.5	
V/(V+Ni) ³	< 0.46	0.46 – 0.60	0.54 – 0.82	> 0.84
U/Th ⁴	< 0.75	0.75 – 1.25	> 1.25	

^{1,2,4} Jones and Manning (1994)

² Dill et al. (1988)

³ Hatch and Leventhal (1992)

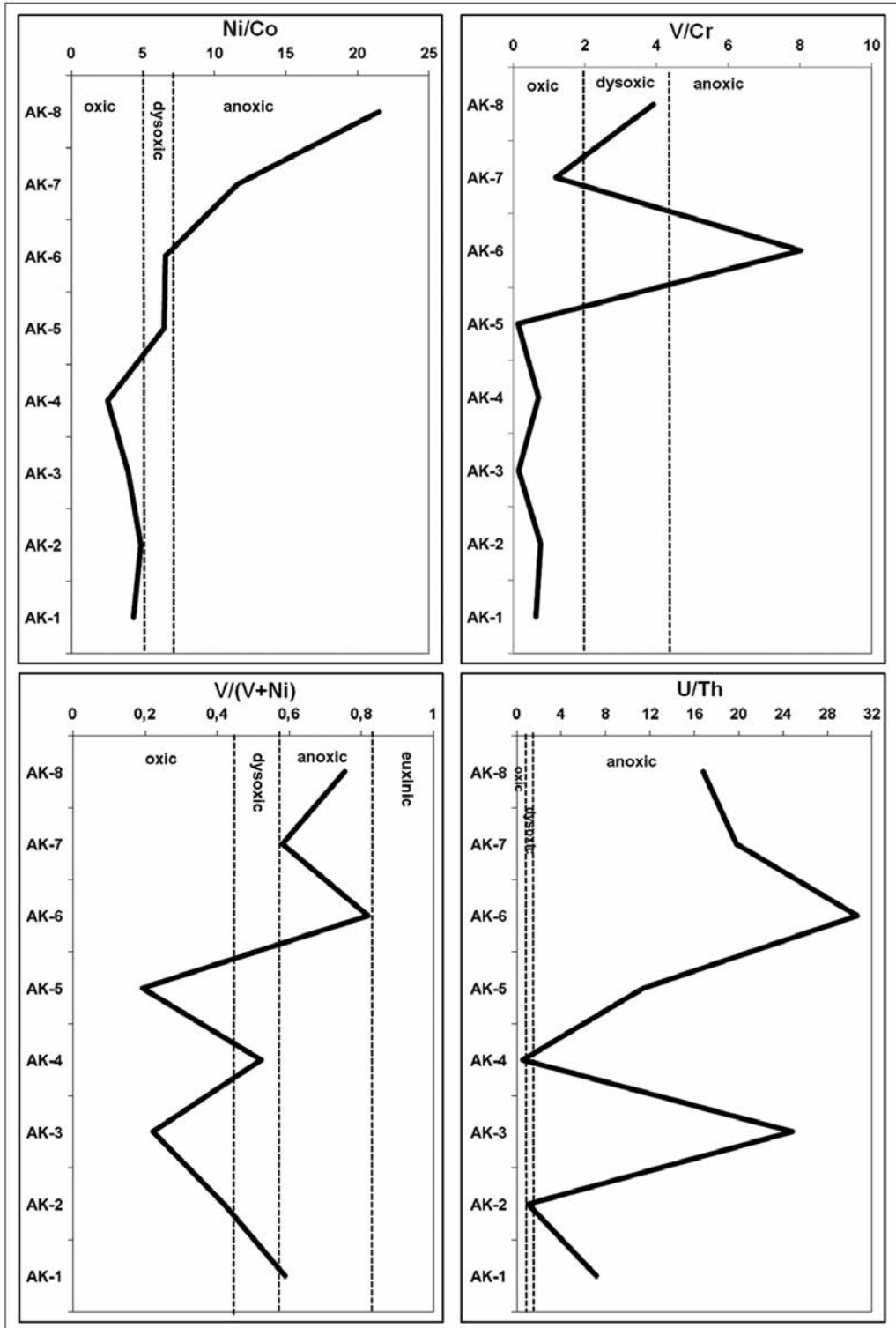


Figure 4- Paleoredox conditions of Akkuyu formation samples

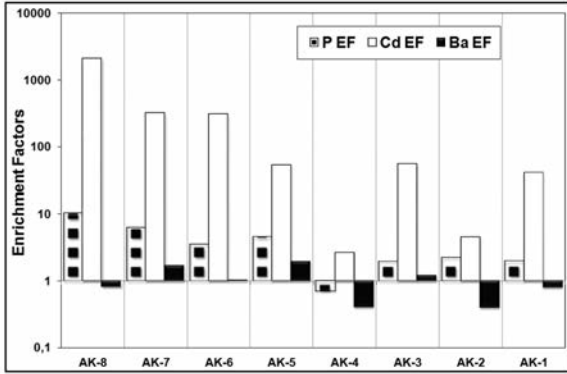


Figure 5- Cd, P and Ba enrichment factors

the Akkuyu formation ($r=0.88$; $R^2=0.78$) implies that primary paleoproductivity of the unit is high (Figure 6).

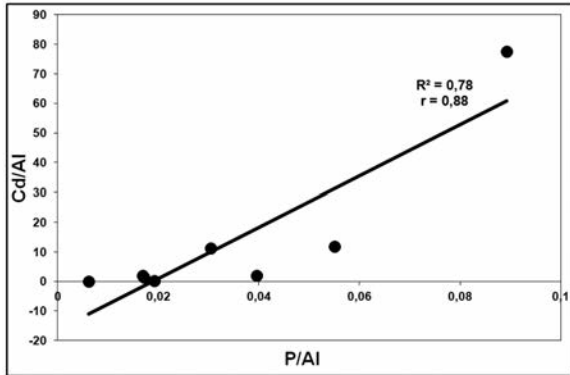


Figure 6- Relationship between Cd/Al and P/Al

Major Element Investigations in the Akkuyu formation

Major oxide compositions of samples are shown in table 2. CaO is the most abundant major oxide with a concentration range from

11.36 to 57.80%, excluding sample AK-4 (5.81%). In shales CaO content is 1-10% and rocks with high CaO content (25-75%) are generally categorized as marl. Ca in rocks is derived from Ca-rich plagioclases and particularly carbonates (e.g. calcite and dolomite). Calcium is also found in some clay minerals, gypsum and anhydrite. SiO₂ concentration in sample AK-4 is 48.83% and it ranges from 2.73 to 36.52% in other samples.

SiO₂ content in fine-grained rocks is controlled by silicate minerals but particularly quartz which is the main constituent of most shales and mudstones. Al₂O₃ concentration in sample AK-4 is 15.13% and it ranges from 0.76 to 9.99% in other samples. Al₂O₃ is particularly associated with the abundance of feldspar and clay minerals (Boggs, 2009). Since shale and marl are composed of the mixture of three major oxides – SiO₂ (detrital quartz and/or biogenic silica), Al₂O₃ (clay fraction) and CaO (carbonate content) – lithology of the samples can be investigated on the SiO₂-Al₂O₃-CaO triangular diagram (Table 2; figure 7). The diagram in figure 7 shows that samples tend to plot close to carbonate corner rather than detrital and clay fraction indicating that, with the exception of samples AK-4 and AK-2, all other samples are represented by the marl lithology.

Akkuyu samples have K₂O content of 0.26 – 2.85%, Mg content of 0.26 – 8.75% and Na₂O content of 0.09 –1.04% (Table 2). In average shale concentrations of both K₂O and MgO are less than 5%. K and Mg contents of shales and mudstones are greatly affected by clay minerals. In addition, Mg and K contents increase with in-

Table 2- Major oxides (%) and trace elements (ppm) values of study area samples

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	V	Cr	Ni	Cd	U	Th	Co	Rb
AK-8	4.57	1.59	0.76	0.23	30.99	0.12	0.75	0.17	0.17	0.003	1011.66	259.31	328.09	65.5	15.1	0.9	15.26	12.62
AK-7	5.01	1.34	0.63	0.04	46.40	0.10	0.66	0.08	0.09	0.003	216.78	182.00	155.68	8.4	17.8	0.9	13.37	14.08
AK-6	7.13	1.47	0.53	0.49	49.32	0.09	0.50	0.08	0.05	0.002	570.25	71.16	125.42	8.8	18.4	0.6	19.03	15.36
AK-5	2.74	0.76	0.24	0.25	57.80	0.09	0.30	0.05	0.04	0.003	14.56	117.00	61.22	0.8	10.3	0.9	9.44	7.22
AK-4	48.83	15.13	5.88	3.01	5.81	0.23	2.85	0.77	0.11	0.048	147.88	207.31	135.72	0.8	7.6	14.5	52.93	131.95
AK-3	3.65	1.01	0.34	0.19	56.24	0.09	0.38	0.05	0.02	0.004	15.68	106.74	54.85	1.1	14.9	0.6	13.84	10.24
AK-2	36.52	9.99	6.43	8.75	11.36	1.04	1.56	0.52	0.23	0.137	136.68	177.21	189.62	0.9	7.5	7.5	38.93	66.02
AK-1	2.93	1.38	0.54	0.26	56.72	0.09	0.26	0.12	0.03	0.005	64.98	101.95	45.50	1.1	8.6	1.2	10.46	8.05

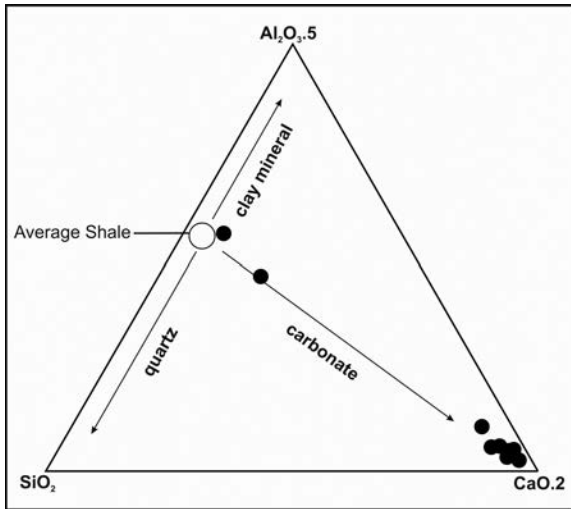


Figure 7- $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ ternary diagram (Brumsack, 1989)

creasing dolomite and K-feldspar abundances, respectively. Shales with $>5\%$ K_2O are quite rare. In other words, high K content of shales is closely related to presence of authigenic K-feldspar. The average Na_2O concentration in shales is about 1-3%. Na content is controlled by both smectite and Na-plagioclase. Fe_2O_3 content in the studied samples is in the range of 0.24 – 6.43%.

Iron is incorporated into iron-oxide minerals (hematite, limonite, and goethite), some micas (biotite, smectite and chlorite), clay minerals and carbonate minerals (siderite, ankerite). Furthermore, in some organic-carbon rich shales significant amount of iron exists in sulfide minerals (pyrite, marchesite).

Petrographic/microscopic methods and XRD determinations are effective tools for classification of rocks. In this respect, petrographic and XRD analyses of samples were carried out. Results of petrographic studies yield that samples are of micritic-sparitic packstone, mudstone and grain stone and show oil indication. Matrix is composed of micrite and less amount of sparite. Whole rock XRD determinations reveal that sam-

ples are composed of calcite, quartz, kaolinite, anorthite, illite and muscovite.

$\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ ratios are also used for classification of sedimentary rocks (Pettijohn et al., 1987; figure 8). $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$ ratio reflects clay and feldspar contents and quartz abundance (Potter, 1978). Based on Pettijohn et al. (1987) diagram, among the studies samples, samples AK-1, 3, 5 and 6 with CaO content above 47% are in the shale field while samples AK-2, 4, 7 and 8 with CaO content less than 47% are plotted in the wacke field. Among the methods used to classify detrital sedimentary rocks, the one based on Ca-enrichment shows the effectiveness of chemical processes in formation of rocks.

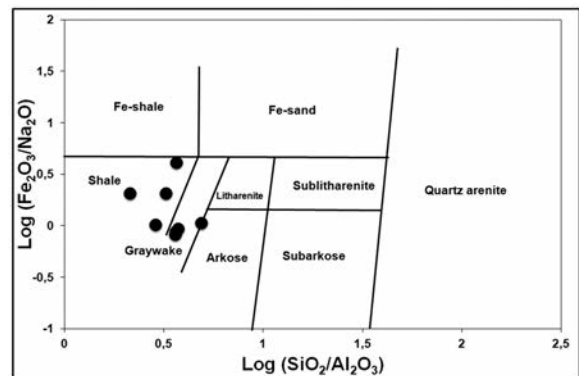


Figure 8- $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ versus $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$ diagram (Pettijohn et al., 1987)

Determination of source by major oxides

Al_2O_3 content of the samples is strongly and positively correlated with SiO_2 , Fe_2O_3 , TiO_2 and K_2O (Table 3, figure 9). This may indicate that SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and K_2O are derived from the same source and their source region is most probably detrital materials transported to the basin. However, as shown from table 3, there are strong negative correlations between CaO which represents for carbonate lithologies and SiO_2 , Fe_2O_3 , Al_2O_3 , MgO and K_2O which repre-

Table 3- Correlations between major oxides

	C _{org}	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃
C _{org}	1,00	-0,26	-0,29	-0,16	0,02	-0,12	0,13	-0,22	-0,21	0,54	0,01	0,49
SiO ₂		1,00	1,00	0,97	0,75	-0,92	0,62	0,96	0,98	0,57	0,76	0,39
Al ₂ O ₃			1,00	0,95	0,70	-0,91	0,57	0,98	0,99	0,54	0,71	0,42
Fe ₂ O ₃				1,00	0,89	-0,92	0,79	0,89	0,95	0,70	0,89	0,41
MgO					1,00	-0,74	0,98	0,58	0,69	0,77	1,00	0,25
CaO						1,00	-0,65	-0,92	-0,94	-0,82	-0,75	-0,68
Na ₂ O							1,00	0,43	0,56	0,79	0,98	0,23
K ₂ O								1,00	0,98	0,53	0,59	0,53
TiO ₂									1,00	0,59	0,70	0,49
P ₂ O ₅										1,00	0,77	0,73
MnO											1,00	0,27
Cr ₂ O ₃												1,00

sent for detrital materials. Strong positive correlations between Al₂O₃ vs. SiO₂-Fe₂O₃-TiO₂-K₂O also reflect association of these elements with clays.

SiO₂ is also strongly and positively correlated with MnO (r=0.76), MgO (r=0.75), Na₂O (r=0.62) and P₂O₅ (r=0.57) (Table 3, figure 9). Silica incorporating into sedimentary rocks is mostly of terrestrial origin. Detrital silicates maybe derived from both silica (e.g. quartz) and biochemical constituents (e.g. radiolarite, diatom and spicules). In marine environments, chert might be precipitated from silica in hydrothermal solutions. Strong and moderately strong correlations between SiO₂ and MnO-MgO-Na₂O-P₂O₅ in the studied samples indicate that these elements are of terrestrial origin and most probably transported to the basin as detrital constituents.

The presence of a negative correlation between Al₂O₃ and CaO (r= -0.91) implies that these two elements are derived from different sources (Table 3, figure 9). As known, Al₂O₃ is of terrestrial origin whilst CaO is derived from carbonates. The abundances of terrestrial elements Al₂O₃, SiO₂, Fe₂O₃, MgO, MnO, K₂O and TiO₂ are very low but CaO contents are generally high.

The fact that Late Jurassic Akkuyu formation is mostly comprised by micrites which are accompanied by oil shales might indicate that the unit was deposited in a restricted carbonate platform in the central Taurids.

Al₂O₃ vs. TiO₂ plots for most clastic rocks are commonly used to determine source rock composition. In the Al₂O₃-TiO₂ diagram (Amajor, 1987) basaltic and granitic source rocks were discriminated (Figure 10).

Al₂O₃ vs. TiO₂ diagram shows that source material of most samples is in basalt composition while composition of samples AK-2 and AK-4 is in the range of granite to basalt. Although in the Al₂O₃-TiO₂ diagram samples are clustered at the beginning of basalt curve, in K₂O-Rb graphic (Figure 17) two samples (AK-2 and 4) are represented by acidic+intermediate composition and other 6 samples are plotted in the basic composition field indicating that samples are mostly of basaltic composition. The Al₂O₃/TiO₂ ratio is 3-8% for mafic magmatic rocks, 8-21% for rocks of mixed composition and 21-70% for felsic rocks. The Al₂O₃/TiO₂ ratio which includes rocks with intermediate composition also reflects Ti-bearing mafic phases derived from felsic and basic rocks (Table 4).

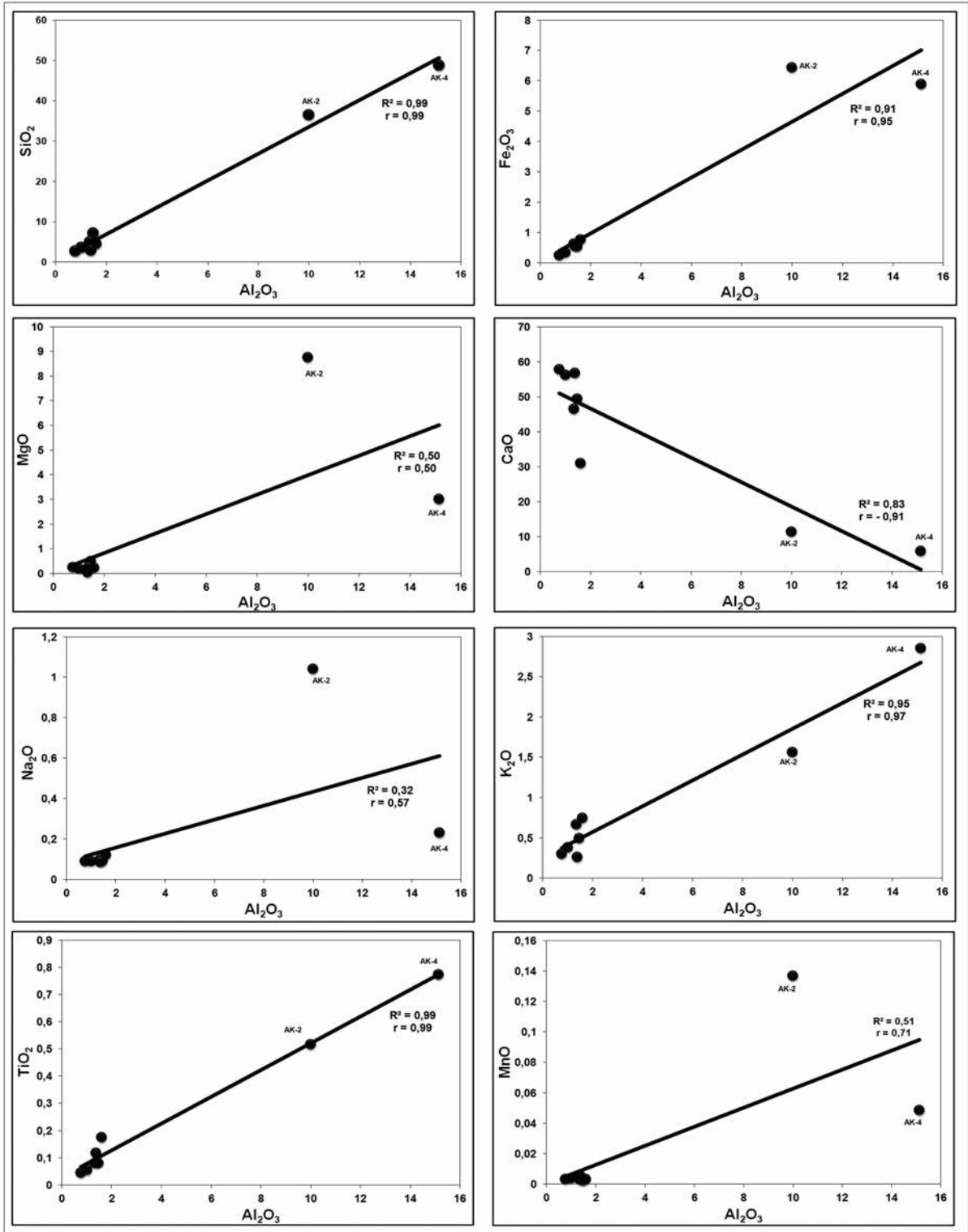


Figure 9- Relationship between Major oxides and Al_2O_3

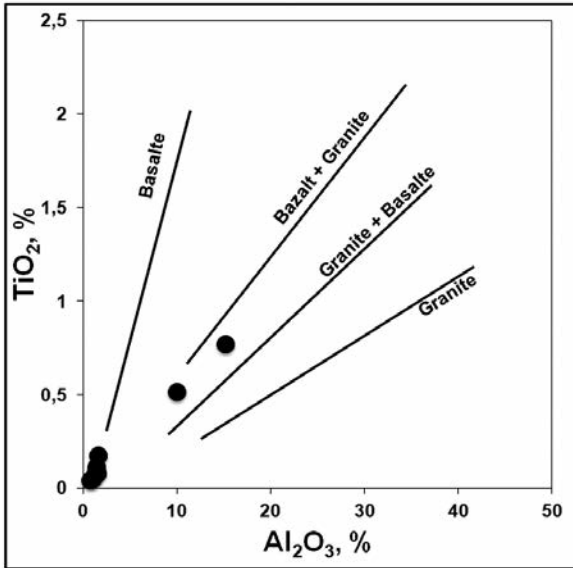


Figure 10- TiO₂ versus Al₂O₃ diagram

Strong correlation between Cr and Ni and high concentrations of these elements were used by several authors to determine source of the sedimentary rock changing from mafic to ultramafic (Hiscott 1984; Garver et al., 1994, 1996). Cr and Ni concentrations in shales reflect Cr and Ni incorporation into clay particles during the course of weathering of chromite other Cr- and Ti-bearing minerals in the ultramafic rocks (Garver et al., 1996). In the studied samples Cr-Ni pair shows strong and positive correlations

Table 4- Al₂O₃/TiO₂ ratio of Akkuyu formation samples

Sample	Al ₂ O ₃ /TiO ₂
AK-8	9,15
AK-7	16,71
AK-6	18,28
AK-5	16,86
AK-4	19,57
AK-3	18,66
AK-2	19,35
AK-1	11,75
Mafic Magmatic	3 – 8
Intermediate	8 – 21
Felsic	21 – 70

(r=0.82; figure 11). High Cr content in samples is most probably derived from variations in source composition and detrital materials of intermediate/basic composition (Floyd and Leveridge, 1987).

Investigation of chemical weathering during the Jurassic-Cretaceous period

Weathering is described as a complex interaction of physical, chemical and biotic processes which alter and disintegrate the rocks at the surface or close to the surface (Selby, 1993). Chemical weathering indices are

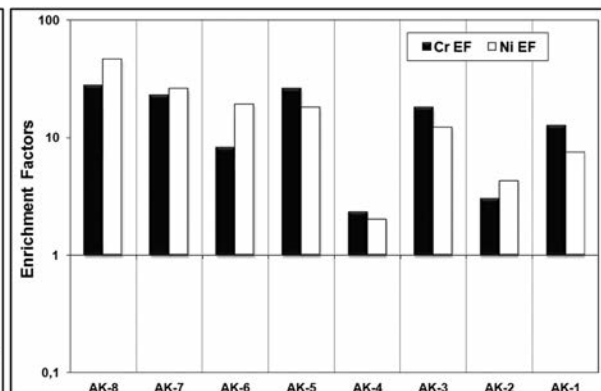
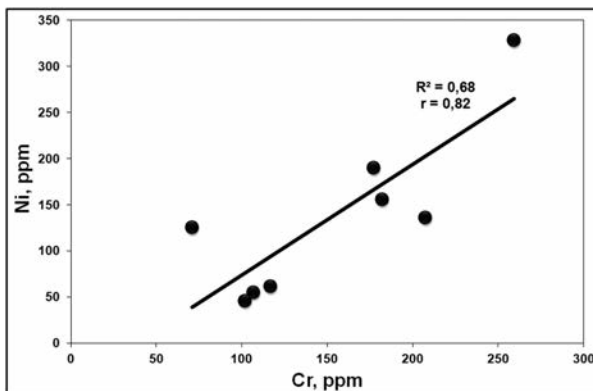


Figure 11- Correlation and element enrichments of Cr and Ni

commonly used in recent and old weathering profile studies (Kirschbaum et al., 2005; Goldberg and Humayun, 2010). Weathering index and chemical alteration index are used to measure the degree of weathering of the terrestrial land from which sediment grains are derived. The degree of compositional maturity of shales can be estimated from the weathering index graphic (Kronberg and Nesbitt, 1981).

In the erosion index graphic the constructed plotting $(\text{Na}_2\text{O} + \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O})$ vs. $(\text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O})$, Akkuyu samples are generally within the illite, Ca-feldspar and Na-feldspar fields (Figure 12). This indicates that feldspars are altered to clay

minerals and K_2O deriving from altered feldspars is captured by Na_2O in illite, smectite and montmorillonite (Kronberg and Nesbitt, 1981).

Using weathering indexes of CIW (Harnois, 1988), CIA (Nesbitt and Young, 1984, 1989), PIA (Fedo et al., 1995) and V (Vogt, 1927), weathering of source rock can be investigated. Data computed based on these indices for the Akkuyu formation are given in table 5. Examination of weathering and alteration ranges reveals that CIW values of Akkuyu samples are indicative of strong chemical weathering while CIA values yield moderately chemical alteration and PIA values indicate a strong alteration (Table 5; figure 13).

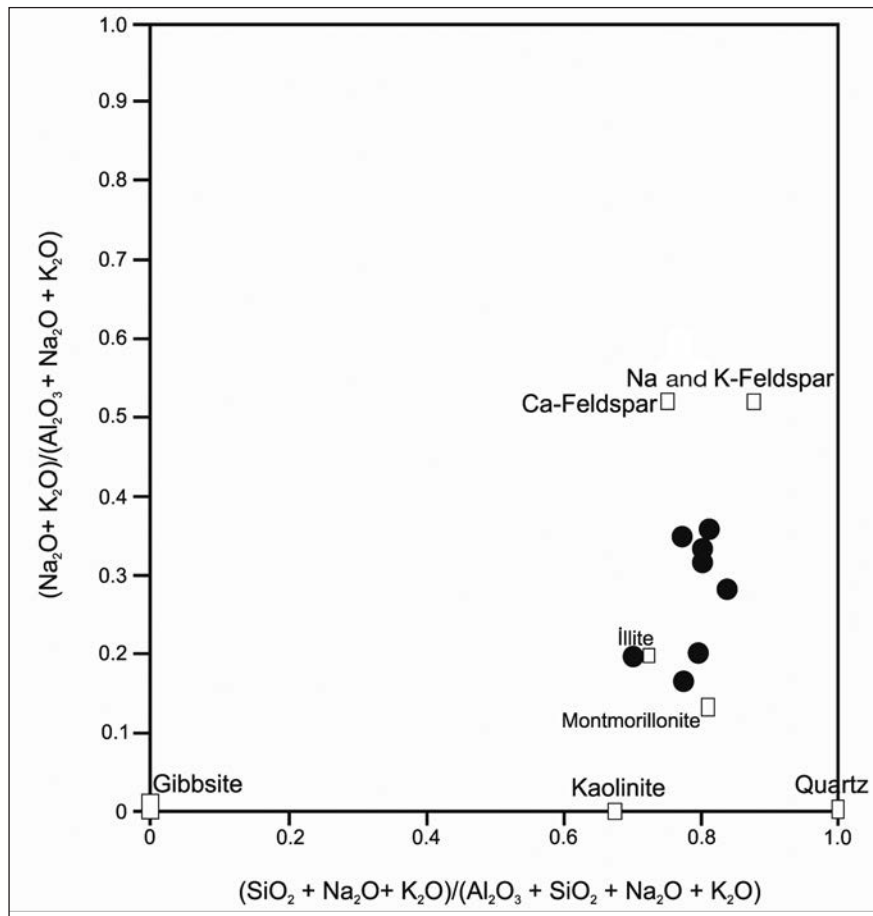


Figure 12- Graphic of Weathering Index (Kronberg and Nesbitt, 1981)

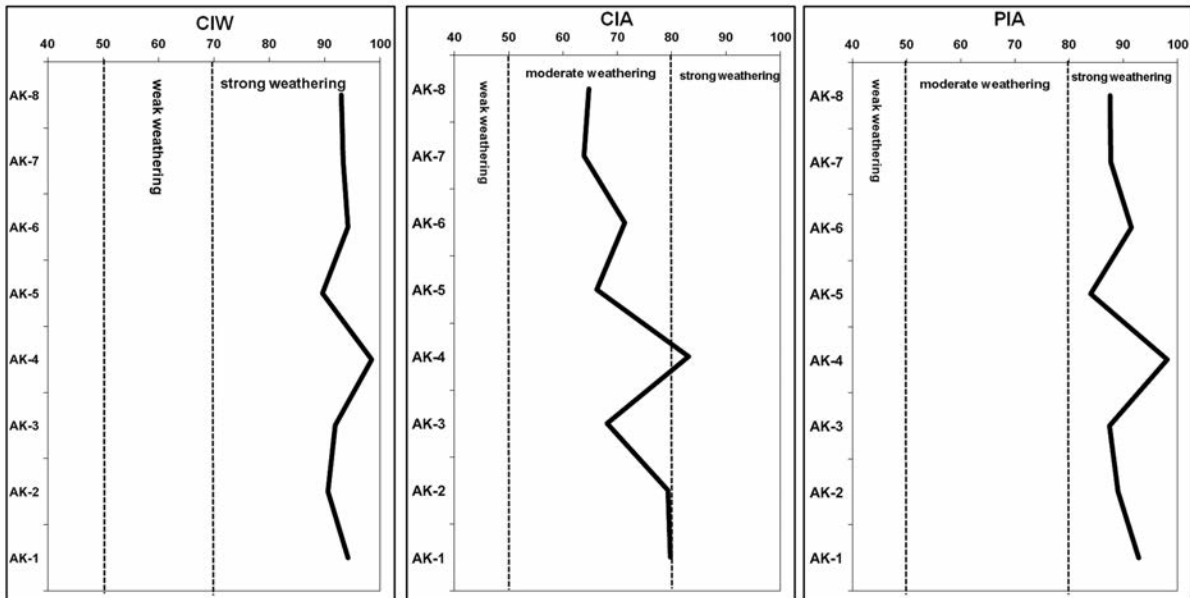


Figure 13- Weathering index of Akkuyu formation samples

Vogt Residual Index (V)

Vogt (1927) suggested a method for evaluating residual sediment maturation which is known as Vogt Residual Index. Roaldset (1972) used this index to determine weathering status of clays in Quaternary deposits in the Numedal region, Norway. Roaldset (1972) used “V” index to compare whole rock chemistry of moren and marine clay deposits and concluded that moren clays are more weathered than marine clays. Vogt Residual Index values indicate that Akkuyu

samples are represented by weathering indexes ranging from weak to strong (Figure 14).

Table 5- Averages of CIW, CIA ve PIA weathering index of studied samples

Sample	CIW	CIA	PIA
AK-8	93,00	64,82	87,61
AK-7	93,39	63,86	87,70
AK-6	94,22	71,42	91,51
AK-5	89,65	66,27	84,01
AK-4	98,50	83,09	98,16
AK-3	91,87	68,11	87,52
AK-2	90,57	79,34	89,02
AK-1	94,18	79,82	92,90

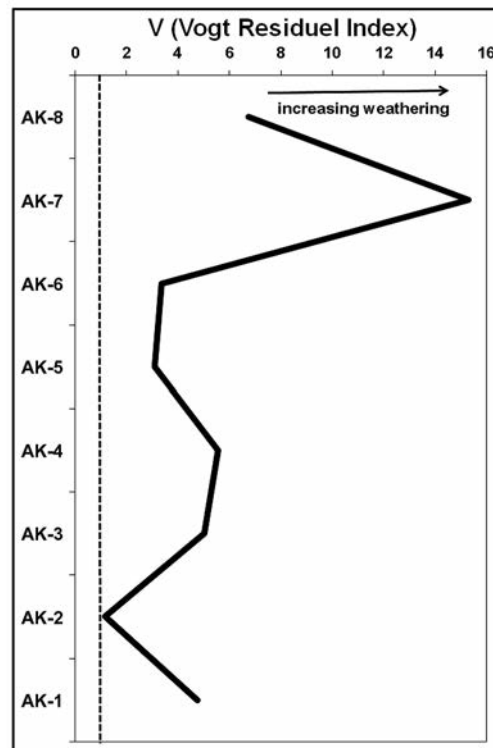


Figure 14- Vogt Residual Index Results of Akkuyu formation samples

Hot and humid climates accelerate alteration of less stable minerals and rock fragments whereas cold and very dry climate regimes facilitate preservation of more stable components. In addition, low relief and slightly inclined topography raises chemical weathering due to slow erosion of landscape by the particles. In the contrary, high relief and steep slopes result in rapid erosion then significant weathering. Sethie et al. (1998) stated that Na, Mg, Ca, U and Rb are easily affected by weathering and diagenesis while rare earth elements (REE) are highly resistant to alteration and fragmentation during the weathering and diagenesis. Element concentrations in Akkuyu sediment samples seem to be affected by erosion, dissolution and sediment diagenesis. In the studied samples, concentrations of Al_2O_3 , TiO_2 and SiO_2 , which are indicator of terrestrial input, are generally found to be low.

However, high carbonate (CaO) and organic material contents of samples and absence of any data to show lacustrine conditions and facies characteristics of the unit might indicate that the Akkuyu formation was deposited under sheltered reducing conditions.

Tectonic Conditions of Central Taurids Region During The Jurassic-Cretaceous Period

Bhatia (1983) and Roser and Korsch (1986) were used $\text{K}_2\text{O}/\text{Na}_2\text{O}$ vs. SiO_2 ; $\text{SiO}_2/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Na}_2\text{O}$; $\text{Al}_2\text{O}_3/\text{SiO}_2$ vs. $\text{Fe}_2\text{O}_3 + \text{MgO}$ and TiO_2 vs. $\text{Fe}_2\text{O}_3 + \text{MgO}$ diagrams to have information on tectonic regime of the source region of detrital sediments. Studies samples of the Akkuyu formation are generally represented by similar distributions and plotted into fields of active and passive continental margins (Figures 15 and 16).

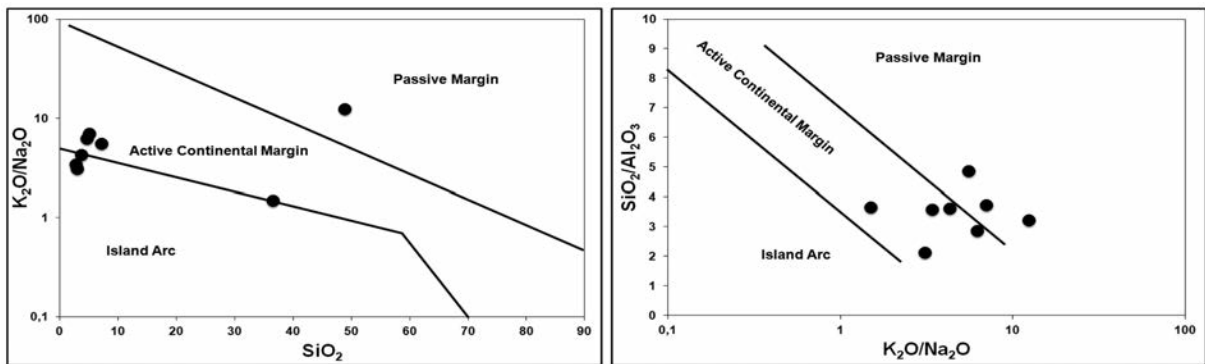


Figure 15- Major and trace elements diagrams for determining tectonic settings (Roser and Korsch, 1986)

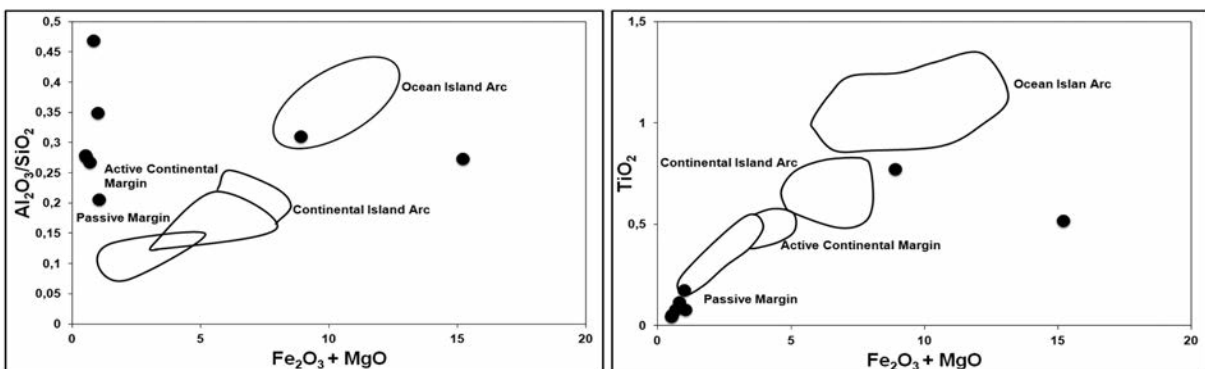


Figure 16- Discriminating tectonic settings diagram by major element compositions (Bhatia, 1983)

Geochemical compositions of sedimentary rocks yield information on tectonic regime of the source region and source rock type of detrital sediments. Considering that most elements are easily redistributed as a result of weathering and alteration, they must be carefully used in source determination. Therefore, trace element or trace element ratios combined with major oxide data are preferentially used for determination of source indicators (Mader and Neubauer, 2004; Gabo et al., 2009). Floyd and Leveridge (1987) used K_2O vs. Rb graphic to discriminate sediments which are derived from rocks of acidic to intermediate-basic composition. In K_2O vs. Rb graphic, rock samples under investigation, with the exception of two samples, mostly show basic rock compositions (Figure 17).

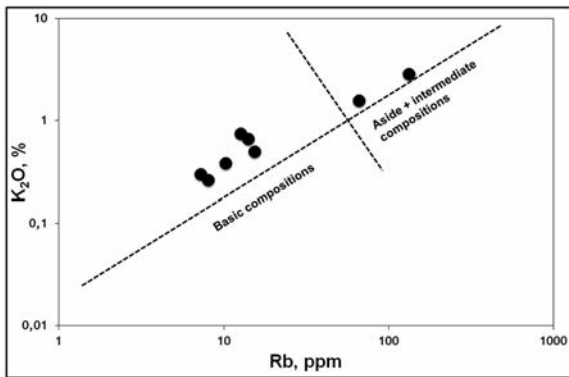


Figure 17- K_2O versus Rb diagram (Floyd and Leveridge, 1987)

Among the samples, K_2O and Rb compositions of sample AK-2 are 1.56% and 66.02 ppm and those of sample AK-4 are 2.85% and 131.95 ppm. K_2O and Rb contents of samples AK-1, 3, 5, 6, 7 and 8 are in the range of 0.26 to 0.75% and from 7.22 to 15.36 ppm, respectively. As shown from TiO_2 vs. Al_2O_3 diagram (Figure 10), most samples are plotted on the basalt axis whereas samples AK-2 and AK-4 are in the basalt+granite and granite+basalt fields supporting the results given above.

RESULTS AND DISCUSSION

- Facies characteristics and a dominant micrite lithology accompanied by bituminous levels imply that the Late Jurassic Akkuyu formation was deposited in a restricted carbonate platform in the central Taurids.

- Based on Hydrogen Index (HI) vs temperature (T_{max} , °C) relation, organic material type of organic material-rich, dark gray and black colored rocks of Akkuyu formation was determined to be Type-III kerogen.

- Redox conditions of Akkuyu formation rocks are found as dioxic-anoxic with respect to Ni/Co ratios, oxic-dioxic and anoxic with respect to V/Cr ratios, oxic and anoxic with respect to V/V+Ni ratios and dioxic and anoxic with respect to U/Th ratios.

- The positive correlation ($r=0.84$) between Cd/Al and P/Al indicates that primary paleoproductivity of the deposition basin is very high.

- According to $SiO_2-Al_2O_3-CaO$ triangular diagram of Akkuyu samples are composed of marl while Si_2O/Al_2O_3 ratio of Pettijohn et al. (1987) and Fe_2O_3/K_2O diagram suggest that samples are represented by shale-sand lithology.

- Results of petrographic studies imply that samples are composed of micritic-sparitic packstone, mudstone and grain stone and show oil indications. Matrix consists of micrite and less amount of sparite. Whole rock WRD determinations showed that samples are composed of calcite, quartz, kaolinite, anorthite, illite and muscovite minerals.

- In the studied samples Al_2O_3 is strongly and positively correlated with SiO_2 , Fe_2O_3 , TiO_2 , and K_2O indicating that rocks might have siliciclastic associations and closely related to clay minerals.

- In order to have information on tectonic regime of the depositional environment of the Akkuyu formation, K_2O/Na_2O vs. SiO_2 ; SiO_2/Al_2O_3 vs. K_2O/Na_2O ; Al_2O_3/SiO_2 vs. $Fe_2O_3 + MgO$ and TiO_2 vs. $Fe_2O_3 + MgO$ diagrams were used. Samples were found to be associated with active and passive continental margins.

- Source rocks of the Akkuyu formation show wide range of composition from basalt and basalt+granite to granite+basalt.

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