VARIATIONS IN MINERAL AND GEOCHEMICAL COMPOSITIONS OF AUTHIGENIC MG-CLAY-BEARING DEPOSITS FROM A NEOGENE LAKE ENVIRONMENT IN SOUTH OF ELAZIĞ, KARABAKIR FORMATION, EASTERN TURKEY

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Abstract: The Neogene shallow-ramp type lake deposit contain Mg-rich clays that were formed by a neoformation processes as a result of the alteration of materials derived from upper Miocene-Pliocene volcanic source rocks. The lake deposit of the upper Miocene – Pliocene Karabakır Formation consists of calcareous sandy claystone, marlstone and limestone intercalated with paleosol horizons. The clayey sandy calcareous rocks of the basin contain significant amounts of Mg-bearing fibrous clay minerals. Lake deposit was analyzed by X-ray diffraction (XRD), ICP-AES and ICP-MS, scanning electron microscopy (SEM). The area is interpreted as a lacustrine environment that underwent variations in depth and paleoclimate, which resulted in range of mineralogical and geochemical changes. Under these conditions, volcanic glass of the Karabakır Volcanics released Si and Mg, which were involved into the formation of Mg-bearing clays. The deposits from the western Rızvanhill section correspond to the shallow part of the lake basin and are characteristically composed of a smectite + palygorskite +calcite mineral association. Paleolake had been expanding and the climate became warm-humid along with the increased paleolake level in Rızvanhill section. In drier paleoclimate, associated with increasing pH, Eh, salinity and alkalinity conditions, the mineral assemblage changes to smectite + sepiolite + dolomite around Bozhill section to the east. Geochemical data also support deepening of the lake system towards the east. The fact that the average ratio of $\sum$ (LREE) $_N$ / $\sum$ (HREE) $_N$ and the (La/Lu)$_{(Nn)(e)}$ enrichment factor are higher for the Rızvanhill section indicates warm-humid paleoclimate and deepening of the lake basin from Rızvanhill to Bozhill Section which experienced drier paleoclimate.

Keywords: alkalinity, sepiolite, palygorskite, authigenic minerals, detrital silicates.

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1. INTRODUCTION

The mineralogical and chemical signature of clay-bearing lacustrine sediments has been successfully used to infer constraints on the paleoenvironmental evolution of sedimentary basins (Leo et al., 2002). It also known that clay minerals vary with respect to the paleogeography of the basin (Jones, 1986; Inglès et al., 1998). pH and ionic concentrations in both surface and pore waters, which can modify the original clay signatures. Several authigenic clay minerals such as Mg-rich smectite, palygorskite and sepiolite can be formed depending on the lake basin depth and variations in alkalinity, salinity and pH (Saez et al., 2007).

Na, Mg, K, Sr, Ca, U and Rb are mobile during the sedimentary processes and therefore have a limited use for understanding sedimentary processes and provenance. On the other hand, several trace elements such as Cr, Co, Th, Sc, Zr, and V should be immobile under depositional conditions and diagnose specific source rocks (Taylor & McLennan, 1985; McLennan et al., 1993). For this reason, like mineralogical changes, geochemical variations have the potential to to help in paleogeographical reconstructions of sedimentary basins (Bauluz et al., 2000; Worash & Valera, 2002; Das et al., 2006, Roy & Smykatz-Kloss, 2007). Although rare earth elements (REEs) generally show similar behaviors and move together in the geological processes, there exist geochemical differences between each element and therefore, they separated and differentiated during the geological reactions in response to the environmental variations, such as during the weathering, transportation, and deposition processes. The differential distribution and concentration of REEs could be used to reconstruct the change in the paleoenvironment and paleoclimate (Zhang, 1998).

The eastern Anatolia region in Turkey witnessed the development of several Miocene-Pliocene lake basins which intercalated with volcanic rocks (Şengör & Yılmaz, 1981, Aksoy, 1993; Alpaslan & Terzioglu, 1996) Investigated sediments are one of these volcano-sedimentary lake basins. This basin has been the subject of various studies. Aksoy (1993) studied the regional geology of the area; Üstündag (1996) described the sedimentological characteristics of this lake deposit. The deepening of lake from west to east has been suggested by Üstündag (1996). Our first findings (Akkoca et al., 2007) reveal that these sediments consist of smectite and some Mg-rich clay minerals such as sepiolite and palygorskite. However, the detailed mineralogical and geochemical characteristics of this lacustrine deposit have not been investigated. The first aim of the present study is to determine and discuss the distribution of Mg-bearing neoformed minerals and the second aim is to evaluate how mineralogy and element geochemistry vary according to the evolution of depositional settings in the basin.

2. GEOLOGY

The basement rocks of the lake basin consist of Permo-Triassic metamorphics, Senonian magmatics, Maastrichtian sediments and middle Eocene-upper Oligocene marine rocks (Fig. 1). Metamorphic rocks exposed in the western part of area are the oldest rock units, and are composed of white colored, intensely fractured marbles and subordinate micaceous clayey schists. The Senonien magmatic rocks are represented by pyroclastic deposits and lavas with a wide compositional spectrum
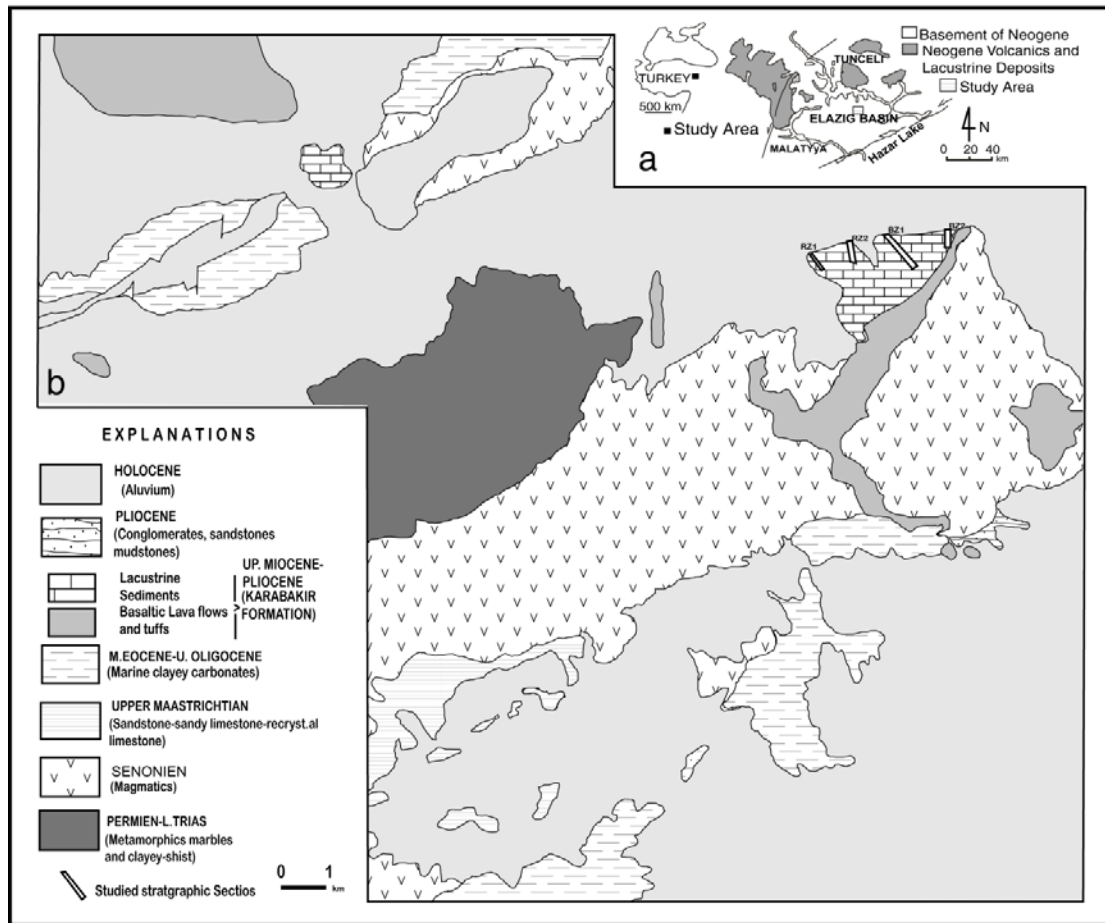
Figure 1. Location (a) and generalized geological map (b) of the study area (From Aksoy, 1993).

Miocene-Pliocene lacustrine volcano-sedimentary units. Lava flows and tuffites of basaltic to andesitic composition that consist of plagioclase, olivine, clinopyroxene and hornblende consist of Karabakır Volcanics. These volcanics interfinger with the studied lake deposits. (Aksoy, 1993; Üstündag, 1996). The studied lake is composed of coarse to fine-grained clastic and carbonate deposits that locally alternate with paleosols. Üstündag (1996) showed that this lacustrine sediment was deposited in a low-energy ramp-type lake and that the lake basin deepened from west (Rızvanhill

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section) to the east (Bozhill section). Red to green colored, loosely cemented claystone alternating with limestone and clayey limestones display thick exposures around Rızvanhill section and they can be interpreted as palustrine deposits (Fig. 2a-b). Limestones around Rızvanhill are mainly white to beige colored, clayey limestones and contain gastropod shells and plant roots. Clayey limestone and limestones display very thick exposures around Bozhill section (Fig. 2c-d). To the southwest of Bozhill section, the basaltic lavas of the Karabakır Formation interfinger with studied lake units and unconformably overlie the Elazığ magmatic rocks. The Pliocene Formation consists of conglomerate, sandstone and mudstones, and the Holocene alluvium deposits are the youngest units in the study area (Fig. 1).

3. MATERIALS AND METHOD

In order to identify the lateral and vertical distribution of clay minerals, three stratigraphic sections were constructed in the lake sediments of the study area (Rızvanhill 1, RZK samples, Rızvanhill 2, RZ samples, Bozhill, BZ samples (Fig. 3). 25 samples were analyzed for their mineralogical characteristics by X-ray powder diffraction (XRD) (Rigaku DMAXIII), with Ni-filtered CuKα radiation, radiation at 15 kV– 40 mA. Samples were scanned from 0 to 60° (2Ɵ) for bulk, and 2-30° (2Ɵ) for clay fraction at a scan rate of 4°/min.

The clay fractions (<2µm) for mineralogical investigations were separated by centrifugation after dispersion. The samples were ground slightly prior to clay extraction in order to prevent clastic micas from entering the clay-sized fraction. The peptizing components of the samples (carbonates)

were removed via acid treatment. The oriented samples of clay minerals were prepared by pipetting the

clay suspension and/or smearing the clay mud onto glass slides. The mineralogical compositions of the
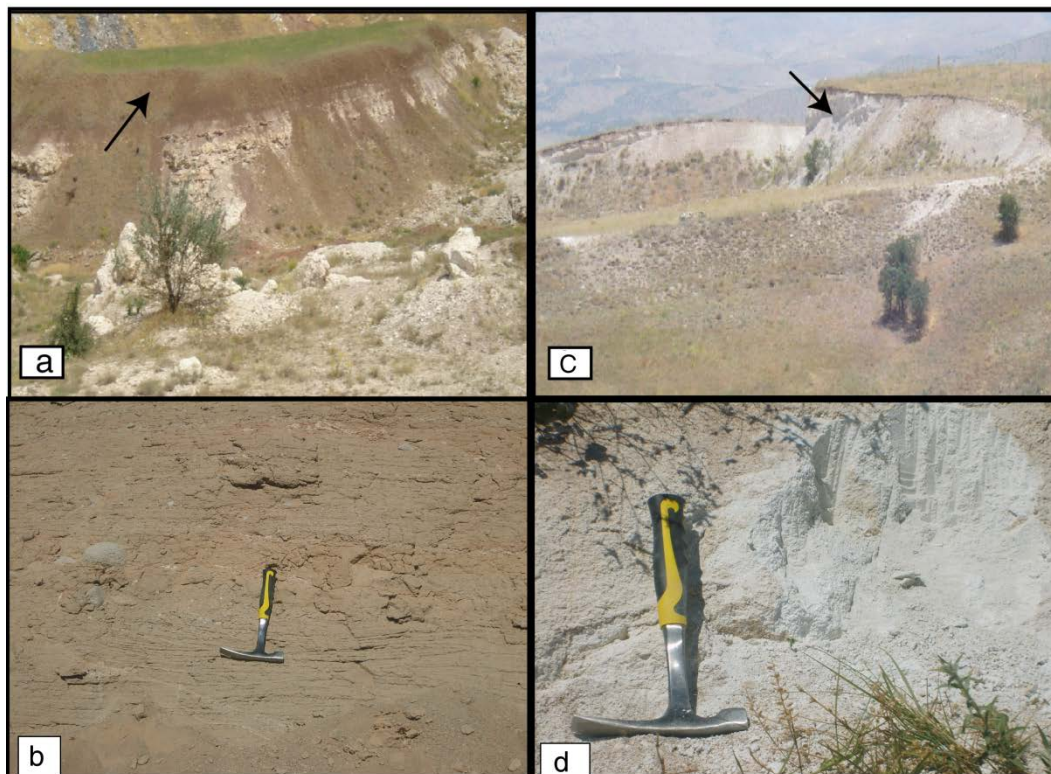

Figure 2. (a-b) Red colored (arrow), loosely cemented claystone levels which are alternated with limestone and clayey limestones from Rızvanhill2 section (c-d) White colored compact, limestones and clayey limestones (arrow) from Bozhill2 section.

clay fractions were assessed by XRD. For these analyses, samples of specific fractions were solvated

with ethylene glycol (EG) at 60 ˚C for 12 h, and subsequently heated to 490 ˚C for 4 h. The assignment

of diffraction maxima was based on the standard JCPS file. The mineral composition of the whole rock

minerals was determined by the technique described by Gündoğdu (1982) after Brindley (1980). In this method, samples were mounted in the same way and the characteristic peak intensities (I) of the minerals were normalized to that of the reflection of dolomite.
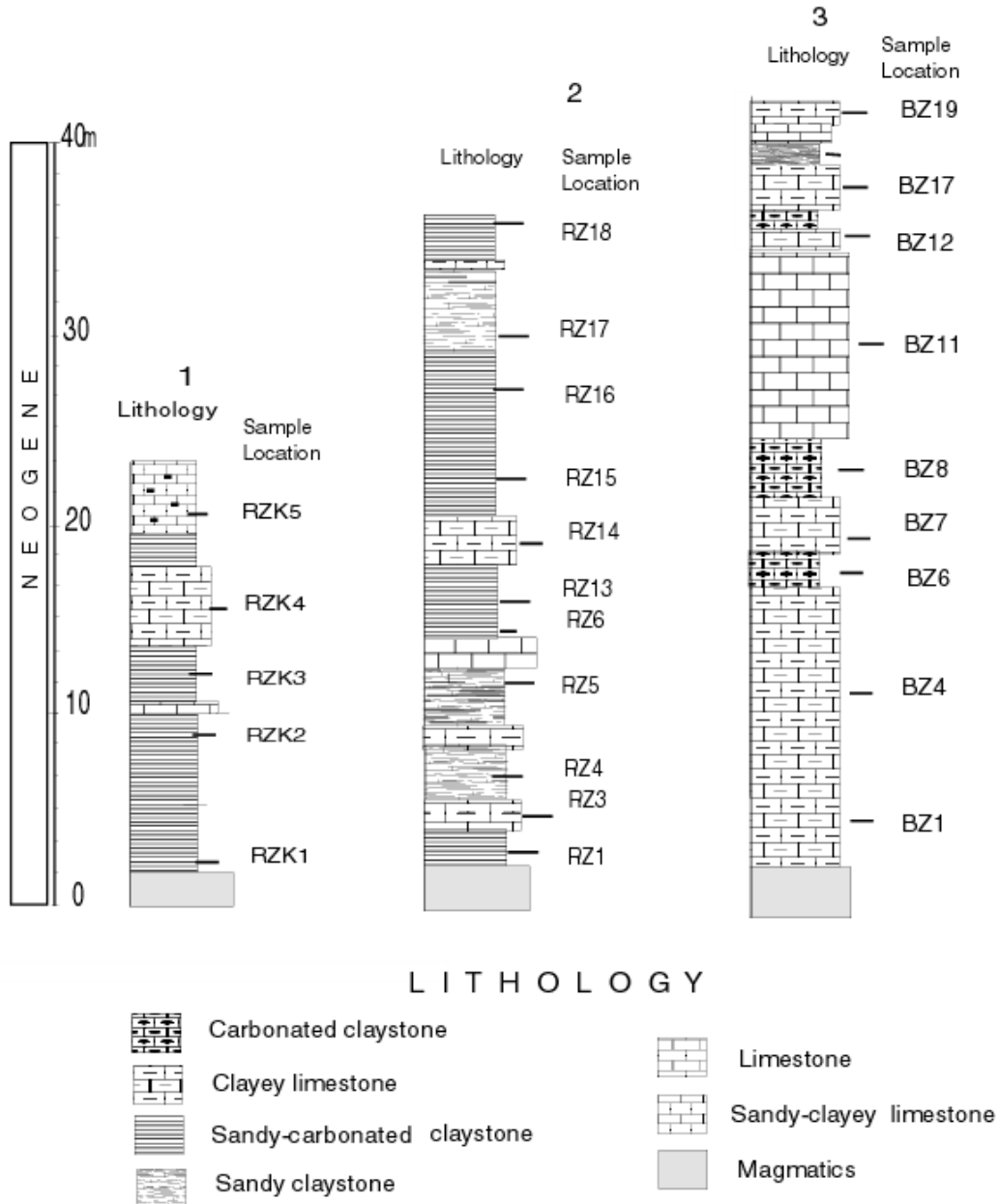

Figure 3. Studied sections from lacustrine succession (1) Rızvanhill 1; (2) Rızvanhill 2; (3) Bozhill Section.

The relative abundance of clay minerals was estimated by weighting integrated peak areas of characteristic basal reflections in the glycolated state with the empirical factors of Yalçın & Bozkaya, (2002) after Gündoğdu, (1982) and Brindley, (1980). The characteristic peak intensities (I) of the minerals were normalized to that of the reflection of kaolinite. Accordingly, the areas of glycolated 15 Å peak were multiplied by 1.57 to yield smectite, the area of 10 peak was multiplied by 1.52 to obtain illite, the 10.50 Å peak areas were multiplied by 1.46 to estimate palygorskite, the 7.8 Å peak areas were multiplied by 6.25 to yield mixed layer clay minerals) smectite-chlorite (S-C), the 3.38 Å peak areas were multiplied by 3.21 to yield mixed layer clay minerals illite-smectite (I-S), the 12.1 Å peak areas were multiplied by 2.69 to yield sepiolite proportions. The relative accuracy of this method is within 15%.

Representative clay-dominated bulk samples were prepared for SEM–EDX, analysis with the LO-435 VP model, by gluing the fresh, broken surface of the sample onto an aluminum sample holder that had been covered with double-sided tape and coated with a thin film (~350 A) of gold, using a Giko ion coater. Minerals were also identified with an Energy Dispersion Spectrometer (EDS) on the SEM.

Chemical data were obtained for 12 representative samples at Acme Analytical Laboratories Ltd. (Canada) using ICP-AES for the determination of major and trace elements and ICP-MS for rare-earth elements (REE). The major, trace and REE concentrations of the collected samples are given in Table 4. Element concentrations were normalized with respect to Al $(E)_N$ (Hassan et al. 1999; Leo et al. 2002), since the concentration of most elements in clayey stones are well correlated with Al_2O_3 and as a result, their concentrations are diluted (Taylor & Mc Lennan, 1985).

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Correlation coefficients were calculated from a data set composed of geochemical analyses, using SPSS 8.0 for Windows. Accordingly, the significance level *(α)* is <0.05.

4. RESULTS

4.1. Mineralogy

4.1.1. XRD Investigation

Clay and calcite are, in similar proportion, the most abundant minerals in all collected samples. Dolomite, quartz, feldspar and opal occur subordinately.

Clay minerals are chiefly composed of smectite, palygorskite lesser amounts of sepiolite, chlorite, illite, I-S, S-C, and kaolinite (Table 1).

The XRD patterns of air dried glycol treatment and heated samples are shown in Figure 4). Disordered Ca-smectites with a broad 15-16 Å peak contain about 15-35% illite layers based on the method of Reynolds, (1980). Smectite is recognized by its 15.5 Å reflection which expands to 17 Å, and then collapses to 10 Å after heating at 550°C. (Figure 4). Typical XRD patterns showed that (001) peak at about 10 Å for illite, (002) peak about 14.5 Å for S-C, (002) peak about 12-12.5 Å for I-S (001) peak at about 10.4-10.5 Å for paligorskite, (001) peak at about 12.1-12.3 for sepiolite and (001) peak at about 7.15-7.20 Å for kaolinite are represented for air dried samples.

Whole rock and clay mineral distributions in samples collected from the Rızvanhill and Bozhill sections are different (Table 1). Smectite is the most abundant clay mineral in samples collected from Rızvanhill section in the western part of the study area and it is accompanied by calcite. Dolomite was detected in small quantities. Quartz and feldspar have higher contents in comparison to Bozhill section (Table 1). Among the clay minerals, smectite+palygorskite are dominant while sepiolite is absent.

Other clay minerals are chlorite, illite, mixed layer clays (illite/smectite, smectite/chlorite) and kaolinite.

Table 1. Average of semiquantitative analysis of mineralogical whole rock and clay minerals from Rızvanhill1-2 and Bozhill stratigraphic sections. Semiquantitative analyses were made by multiplying the intensities of the principal basal reflections of each mineral by suitable factors according to Gündoğdu (1982) and Yalçın and Bozkaya (2002) after Gündoğdu (1982) and Brindley (1980). Paragenesis were determined with average values of minerals in sections. >45% = ++++, 5-45 %=+++ , 2-5%=++, <2% =+ .

	Whole Rock Minerals						Clay Minerals							
	Calc	Quarz	Feld	Dol	Opal	Clay	Smect.	Palig.	Chlori.	S-C/	I-S	İllite	Kaol.	Sepio.
Rızvanhill 1 n=5	+++	++	++	---	+	++++	++++	+++	+++	++	++	++	--	---
Rızvanhill 1 n=11	+++	++	++	+	+	++++	++++	+++	+++	++	++	+++	+	---
Bozhill n=9	+++	+	+	+++	+	+++	+++	+++	+++	++	+++	+++	---	+++

Dolomite has higher amount in samples taken from the Bozhill section further east in the area feldspar, opal and quartz occur in trace quantities. In Bozhill section, sepiolite is also measured. Chlorite, illite and mixed layer clays (illite/smectite, smectite/chlorite) are found in lesser amounts (Table 1).

4.1.2. Scanning Electron Microscope (SEM) Studies

The Mg-rich clay dominant samples by determined by XRD analyses were also studied with scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDS). In SEM studies,
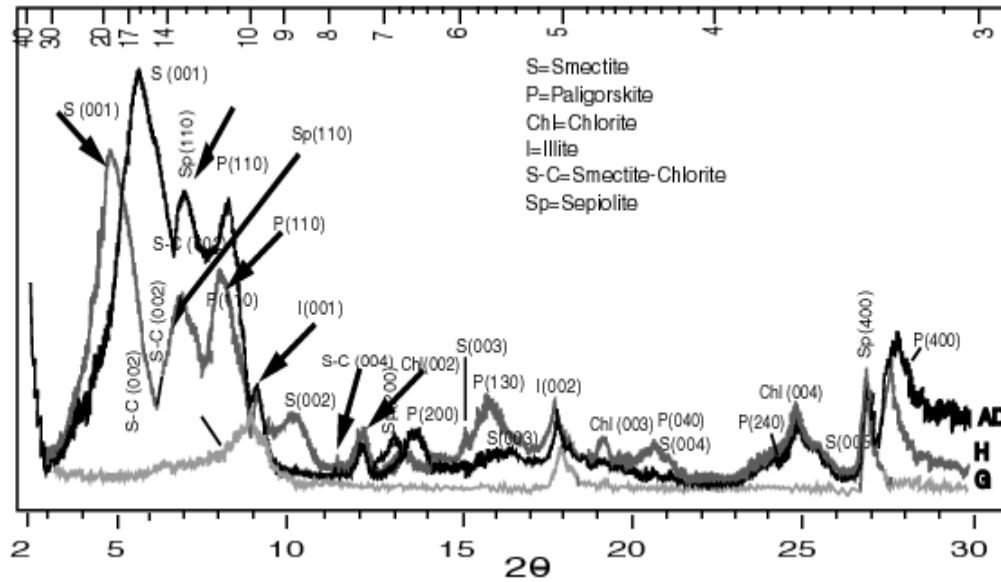

Figure 4. XRD patterns of representative   BZ7 sample. The charactersitic peak intensities (I) (arrow) of each minerals were normalized to that of the reflection of kaolinite for semiquantitative analyses according to Yalçın and Bozkaya, 2002 after Gündoğdu, 1982 and Brindley, 1980).

some morphologic features of sub-microscopic minerals, such as shape and dimension, possible mineral transformations and textural characteristics were recognized.

Smectite crystallites are usually wavy and flaky, often yielding characteristic honeycomb textures . In general, smectite develops in dissolution voids of the volcanic glass (Fig. 5a). Christidis et al., (1995) also indicated that smectite was derived from alteration of volcanic glass and feldspar in Kimolos Island, Aegean, Greece. Very small smectite aggregates are observed to be fluffy (Fig. 5b).
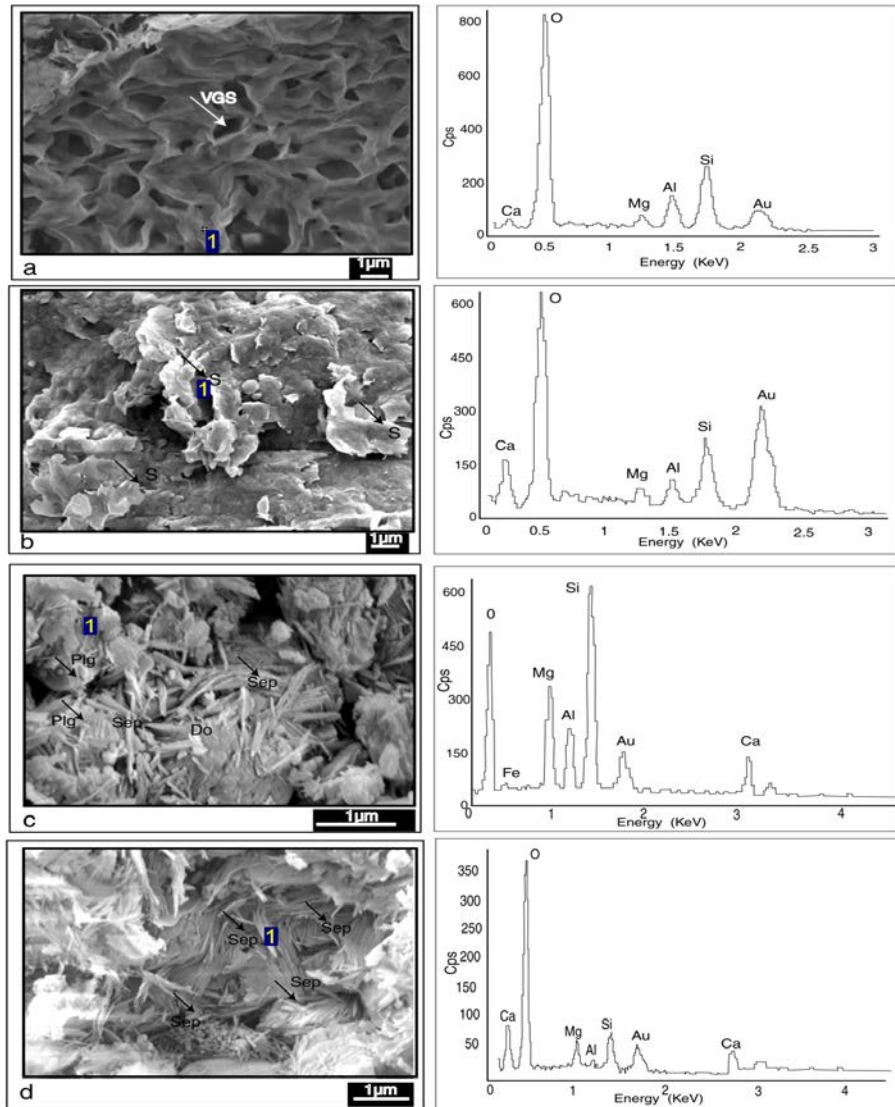
Figure 5. Scanning electron microscope (SEM) photographs and Energy Dispersion Spectrometer (EDS) analysis of (a) Smectite crystals with honeycomb structure.Volcanic glass shards (VGS) developed during smectite formation (RZ3 sample) (b) Fluffy smectite replacing vitric matrix and crystals (*S*) (RZ8 sample). (c) The thin meshworks of fan-like sepiolite (*Sep*) and acicular palygorskite (*Plg*), coating dolomite grains (B17 sample). (d) Fan - like forms of fibrous sepiolites (BZ17 sample).

Palygorskite and sepiolite are seen as fine and filamentous fibers coating dolomite (Fig. 5c). In addition, palygorskite has a tabular shape with smooth edges and the acicular morphology was recognized at the tips of the plates (Fig. 5c). Sepiolite fibers form fan-like bundles. The sepiolite filaments are 0.5-1 µm long with a width and thickness of less than 1µm (Fig. 5c-d). Such features can be considered as textural evidence for authigenic palygorskite-sepiolite (Jones, 1986; Tlili et al., 2010).

4.2. Geochemistry

4.2.1. Major and Trace Elements

Compositional variations of the lake samples are comparatively low (Table 2). Their SiO_2 and Al_2O_3 contents show broad ranges from 4.44% to 45.42 % and from 1.32 % to 13.60 %, respectively, SiO_2 and Al_2O_3 depletion in lake sediments was explained by the dilution due to higher carbonate accumulation (Lepane et al., 2007)

Correlation analysis was performed to reveal any communality of minerals and chemical elements. Some correlation plots for major and trace elements are shown in Figure 6-7. SiO_2 is positively correlated with Al_2O_3, Fe_2O_3, K_2O, Cr_2O_3, TiO_2 and negatively correlated with CaO and MgO. This suggests that CaO and MgO are derived primarily from carbonates, and other elements are associated with silicates (Fig. 6-7). Rb displays positive correlation with K_2O, demonstrating that a similar geochemical behaviour can be associated with illite, since both elements are preferentially illite (Fig. 6) (Das and Haake, 2003). Positive correlations of Ti- and Sc, Ga, Nb- and Ta, Th suggest that Ti- and Nb-bearing minerals may control the distribution of trace elements (Fig. 8). (Taylor & Mc Lennan, 1985; Plank & Langmuir, 1998; Dass et al., 2006; Chester, 1990; Leo et al., 2002). Regarding the Al-

Table 2. Major, trace and REE concentrations of samples. $\chi(E)_N$: Average of Al normalized elements, $\chi \sum (LREE)_N / \chi \sum (HRRE)_N$: the arithmetical average of the ratio of Al-normalized $\sum(LREE)$ to arithmetical average of the ratio of Al-normalized $\sum(HREE)$, $\chi(La/Lu)_{(Nn)(e)}$: $\chi[(La_{sample}/Al_{sample})/ La_{NASC}/Al_{NASC}) / (Lu_{sample}/Al_{sample}) / (Lu_{NASC} / Al_{NASC})]$ (NASC values from Gromet at al., 1984).

	Rızvanhill Samples								
	RZ3	RZ5	RZ8	RZ14	RZ17	RZK1	RZK2	RZK5	$\chi(E)_N$
SiO_2	4.44	10.08	24.5	45.42	53.66	22.09	38.27	23.62	0.74
TiO_2	0.06	0.15	0.37	0.69	0.48	0.34	0.56	0.35	0.05
Al_2O_3	1.32	2.98	7.24	13.6	9.36	6.25	10.60	6.51	1.00
Fe_2O_3	0.73	1.46	3.21	5.96	4.83	3.03	4.76	3.06	0.48
Cr_2O_3	0.005	0.004	0.01	0.019	0.021	0.015	0.028	0.019	0.002
MnO	0.02	0.04	0.07	0.04	0.02	0.04	0.06	0.04	0.007
MgO	0.86	1.19	1.37	1.08	2.92	1.85	2.17	2.08	0.30
CaO	50.1	43.93	28.3	10.1	8.32	32.93	18.92	31.7	8.77
Na_2O	0.03	0.02	0.08	0.08	0.07	0.11	0.10	0.06	0.01
K_2O	0.15	0.22	0.53	0.91	0.89	0.47	0.87	0.48	0.08
P_2O_5	0.04	0.02	0.06	0.05	0.029	0.13	0.07	0.06	0.01
LOI	42,2	39,9	34.18	22.02	19.4	32,6	23,5	32.01	…
Trace elements and REE in ppm)									
Sc	2	4	9	14	12	9	16	11	1.38
V	18	33	77	125	114	73	117	80	11.46
Co	1.7	3.3	21.5	17.2	8.8	11.7	19.4	10.3	1.6
Ni	20	21	48	57	77	72	88	51	6.21
Cu	5.6	9.9	18.6	31.4	41.1	24.3	27.2	18.3	3.26
Zn	10	15	36	61	56	38	52	34	5.53
Ga	1.5	3.3	7.7	13.6	9.7	7.0	11.6	6.5	1.06
Rb	7.2	8.1	23.4	32.9	42.5	18.9	29.3	16.0	3.32
Sr	155	86	90.	139	69	140	194	159	30.31
Y	2.3	9.2	14.8	12.4	6.5	10.9	17.0	14.2	1.75
Zr	15.2	26.9	94.9	111.5	95	50.0	78.0	53.2	9.44
Nb	1.2	1.8	6.5	8.5	7.4	3.9	5.7	5.4	0.72
Ba	37	23	120	94	89	115	154	99	14.6
La	2	6.4	10.5	8.6	6.7	9.3	11.9	9.9	1.32
Ce	4	10.4	22.4	18.4	15.1	16.4	21.8	13.2	2.41
Pr	0.46	1.47	2.7	2.13	1.65	2.05	2.89	2.03	0.30
Nd	2	6.6	10.6	8.1	5.8	8.2	12.6	8.1	1.26
Sm	0.36	1.21	2.35	1.75	1.17	1.83	2.71	1.80	0.06
Eu	0.09	0.36	0.52	0.41	0.24	0.49	0.77	0.57	0.26
Gd	0.39	1.31	2.26	1.75	1.05	1.76	2.83	2.10	0.28
Dy	0.39	1.45	2.4	1.97	1.08	1.77	2.92	2.22	0.05
Ho	0.09	0.26	0.5	0.42	0.24	0.37	0.62	0.46	0.17
Er	0.25	0.81	1.46	1.36	0.73	1.06	1.77	1.35	0.17
Yb	0.24	0.76	1.54	1.4	0.85	1.04	1.83	1.29	0.02
Lu	0.04	0.13	0.23	0.21	0.13	0.17	0.28	0.20	0.39

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Th	0.7	1	3	4.1	4.2	2.7	3.4	2.3	
$\chi\sum$ (LREE)$_N$ /$\chi\sum$ (HRRE)$_N$							7.75		
χ(La/Lu)$_{Nn\,(e)}$							0.94		

	Bozhill Samples				
	BZ4	BZ8	B3	B6	$\chi(E)_N$
SiO_2	50.39	48.08	37.83	31.9	3.57
TiO_2	0.7	0.62	0.55	0.44	0.049

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|					
Al_2O_3	14.34	13.44	10.19	9.16	1.00
Fe_2O_3	6.35	5.77	5.16	4.89	0.47
Cr_2O_3	0.017	0.02	0.029	0.01	0.001
MnO	0.03	0.04	0.07	0.08	0.05
MgO	3.66	5.51	16.12	22.4	1.17
CaO	3.82	9	5.74	4.23	0.49
Na_2O	0.1	0.15	0.07	0.11	0.009
K_2O	1.17	0.95	0.59	0.79	0.07
P_2O_5	0.056	0.069	0.08	0.11	0.01
LOI	19.1	20.1	23.4	25.8	…
Sc	16	16	17	14	1.37
V	149	127	131	124	11.55
Co	15	14	20.7	9.5	1.28
Ni	54	50	74	49	3.83
Cu	32.6	31.8	30.4	34.9	2.85
Zn	59	61	51	68	5.27
Ga	14.3	13.6	10.4	10.7	1.04
Rb	35.3	27.4	19.7	27.	2.35
Sr	71	307	875	592	44.6
Y	12.2	13.9	14.5	15.2	1.24
Zr	118	120.3	77.0	62.8	7.91
Nb	7.5	7.4	4.8	4.6	0.51
Ba	96	89	140	123	10.12
La	6.5	8.6	9.4	9.7	0.76
Ce	16.8	22.8	19.3	15.1	1.6
Pr	1.85	2.43	2.19	2.22	0.19
Nd	7.00	9.8	9.4	10.3	0.81
Sm	1.63	2.18	2.24	2.16	0.18
Eu	0.42	0.54	0.62	0.67	0.05
Gd	1.84	2.26	2.25	2.51	0.19
Dy	1.98	2.58	2.50	2.75	0.21
Ho	0.41	0.52	0.50	0.63	0.046
Er	1.3	1.54	1.51	1.74	0.13
Yb	1.47	1.62	1.59	1.69	0.14
Lu	0.23	0.26	0.25	0.29	0.022
Th	3.6	3.4	2.6	2.5	0.25
$\chi\sum (LREE)_N /\chi\sum (HRRE)_N$		6.55			
$\chi(La/Lu)_{Nn (e)}$		0.44			
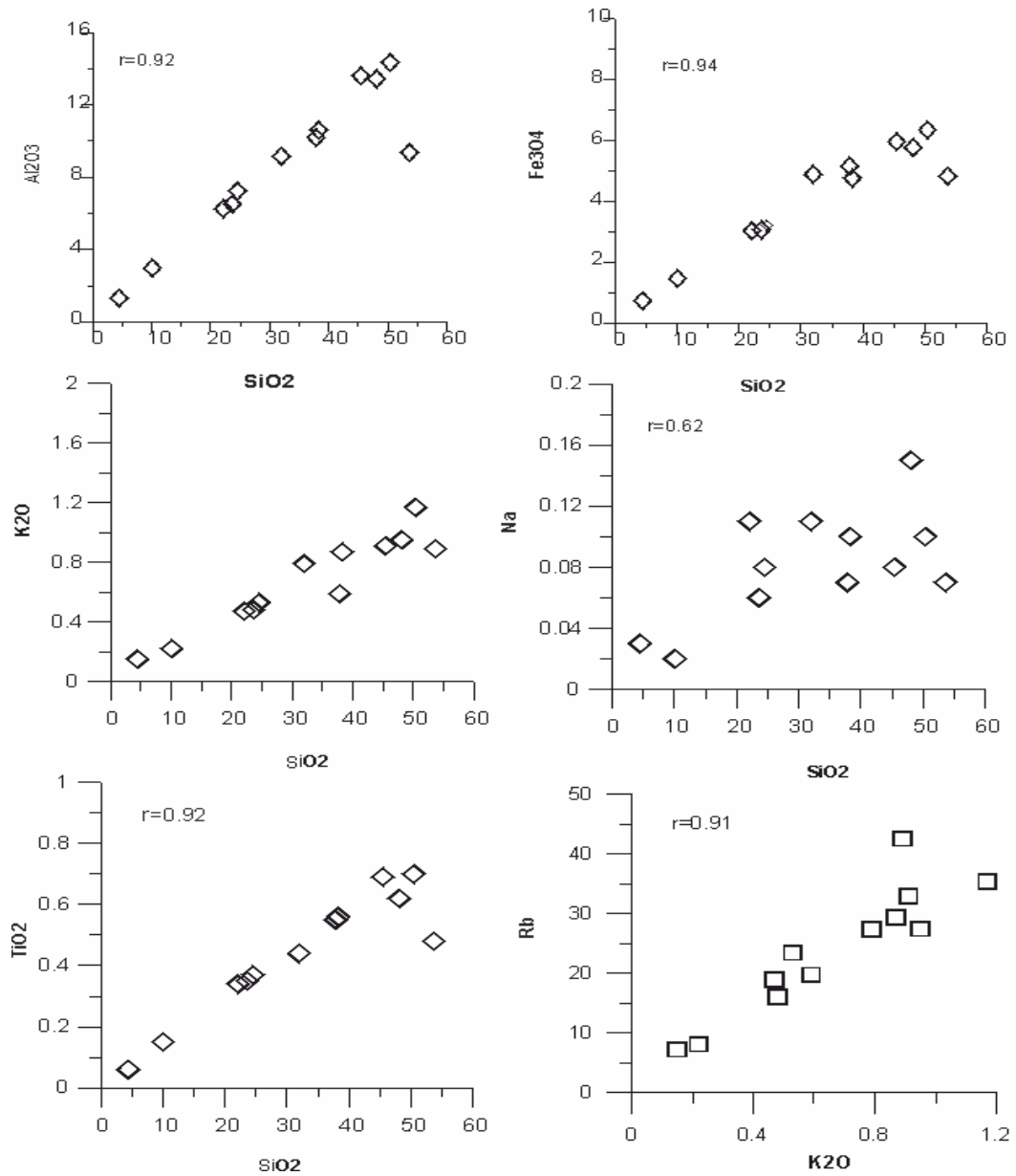
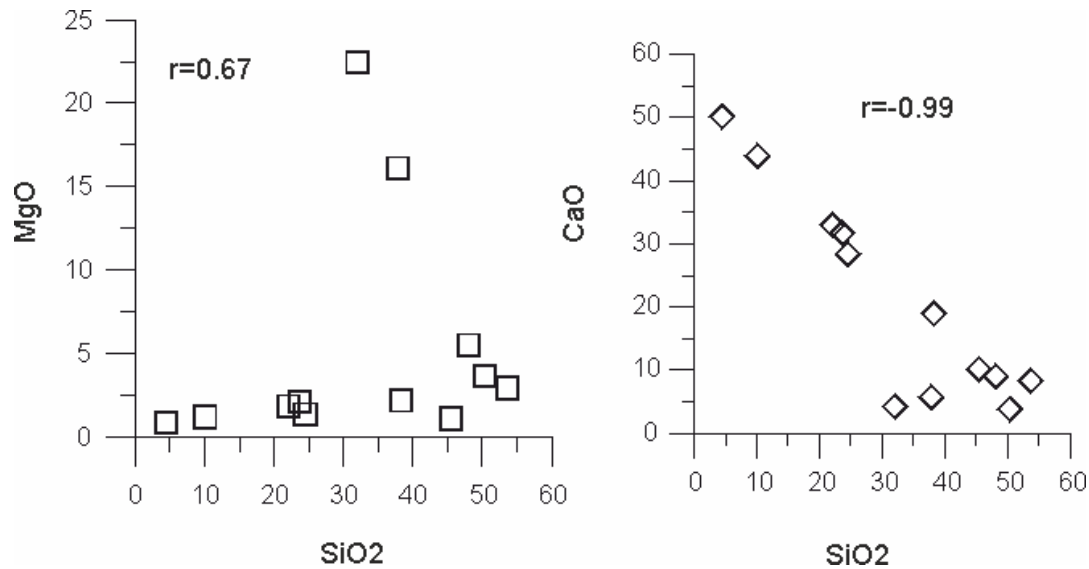Figure 6. Correlation graphics between some major and trace elements. Significance level *(α)* is <0.05.

Figure 7. Correlation graphics between SiO_2 and MgO,CaO elements. Significance level *(α)* is <0.05.

normalized values $\chi(E)_N$ of some major oxides (e.g. SiO_2, Al_2O_3, K_2O, TiO_2, Fe_2O_3 and MnO) and trace elements (e.g. Ni, Sc, V, Ba, Co, Cs, Ga, Hf, Nb, Rb, Ta, Th, U, Zr) concentrations In the Rızvanhill1-2 and Bozhill section compositions reveal slight differences, except for Ca, Mg and Sr (Fig. 9). Similarity between Rızvanhill1-2 and Bozhill samples can be explained by similar source area. The Ca, Mg and Sr differences are due to differences of pH, alkalinity and salinity due to differences of dept and drier paleoclimate.

The geochemical differences between elements such as Th (indicative of a felsic source) and Sc, Co and Cr (indicative of a mafic source) have been exploited to distinguish between felsic and mafic provenance by various authors (e.g. McLennan & Taylor, 1991). Th/Sc, Th/Co, Cr/Th have been used to differentiate sediments derived from different source rocks. (Cullers et al., 1988). These element

ratios of lake sediments are more convenient to values for sediments, derived from mafic source rocks,
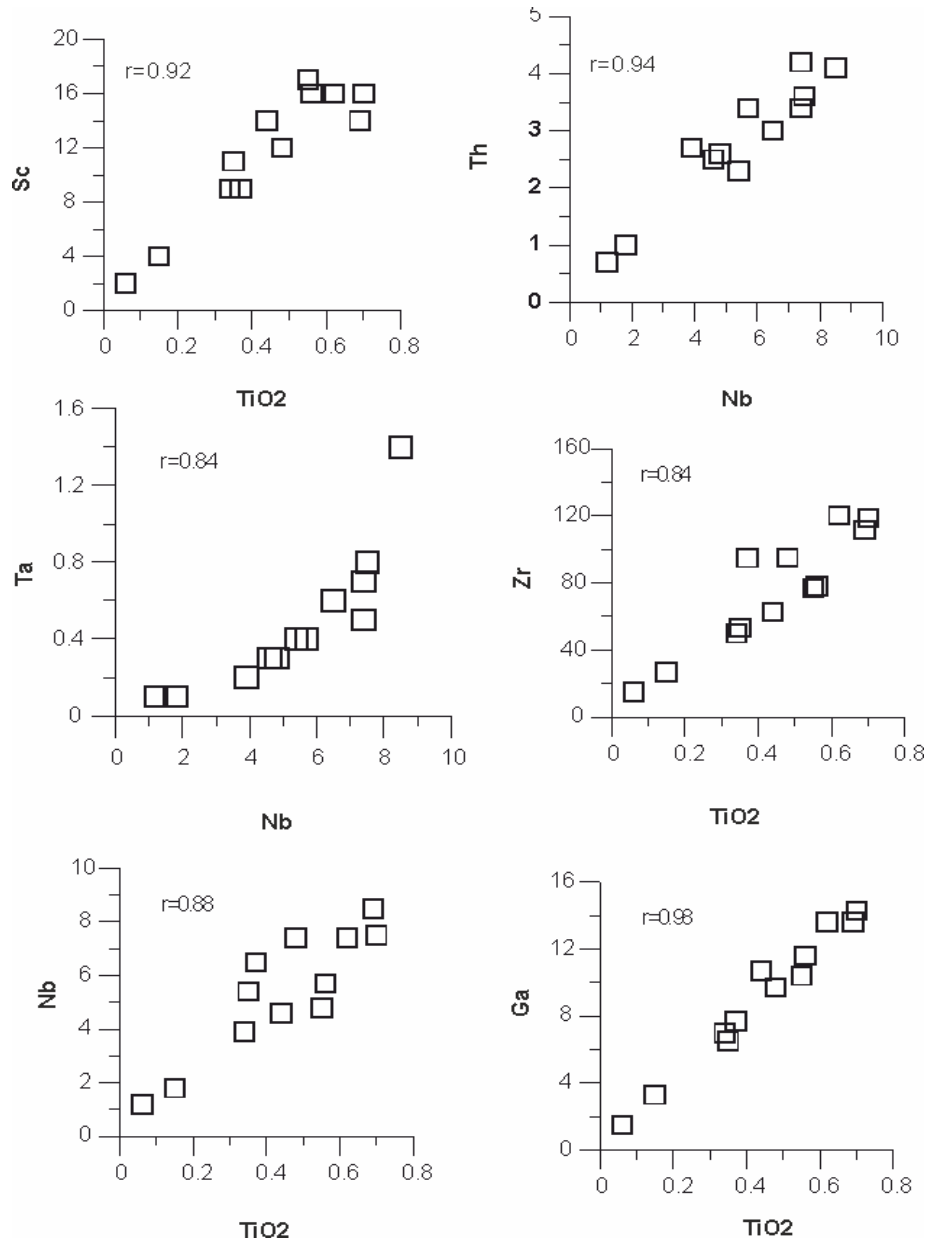
(Table 3).

Figure. 8. Correlation graphics between Ti- Ga, Nb, Zr and Nb, Th, Ta. Significance level *(α)* is <0.05.
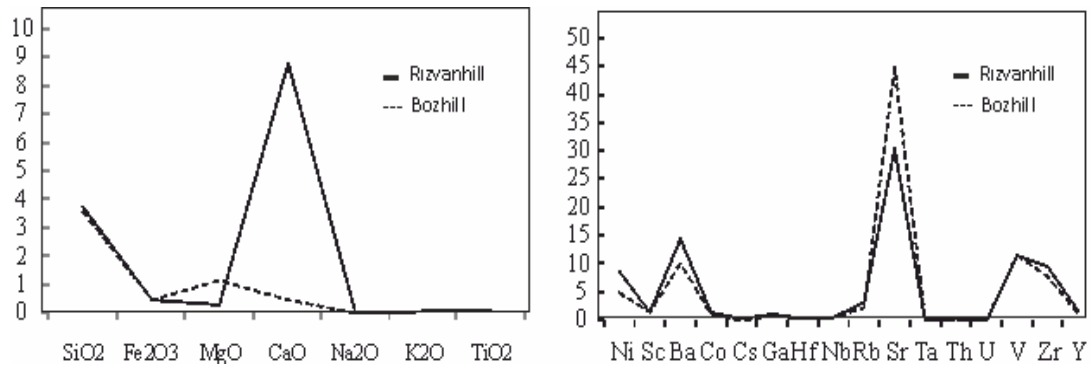
Figure 9. Comparison of geochemistry of Rızvanhill1-2 and Bozhill section

Table 3. Range of elemental ratios in this study, compared the ratios in similar fractions derived from mafic rocks (Cullers 1994; 2000). ,

	Rızvanhill 1-2	Bozhill	Mafic Rocks
Th/Sc	0,20-0,35	0.15-0.22	0,05-0,22
Th/Co	0,13-0,47	0,12-0,24	0,04-1,40
Cr/Th	22.80-56.52	32.30-76.31	25-500

4.2.2. Rare Earth Elements

REEs are especially useful for monitoring source area composition (Taylor & Mc Lennan, 1985; Das et al., 2006). These elements have short residence time in the water column, and thus are transferred almost completely into the sedimentary record and are useful for differentiating felsic from mafic source components in shales (Fedo et al., 1996; Bauluz et al., 2000).

REEs of lake samples are shown at Table 2. Positive correlations between Ti- ∑REE suggest that some Ti- bearing minerals may at least partially control the distribution of certain trace elements (Fig. 10a) (Gonzalez -Lopez et. al., 2005).

The REE concentrations of samples are normalized to chondrite values and it was determined that LREE concentrations are more enriched in comparison to HREEs, and the absence of Eu anomalies shows that lake samples are generally mafic in composition (Fig. 10b).
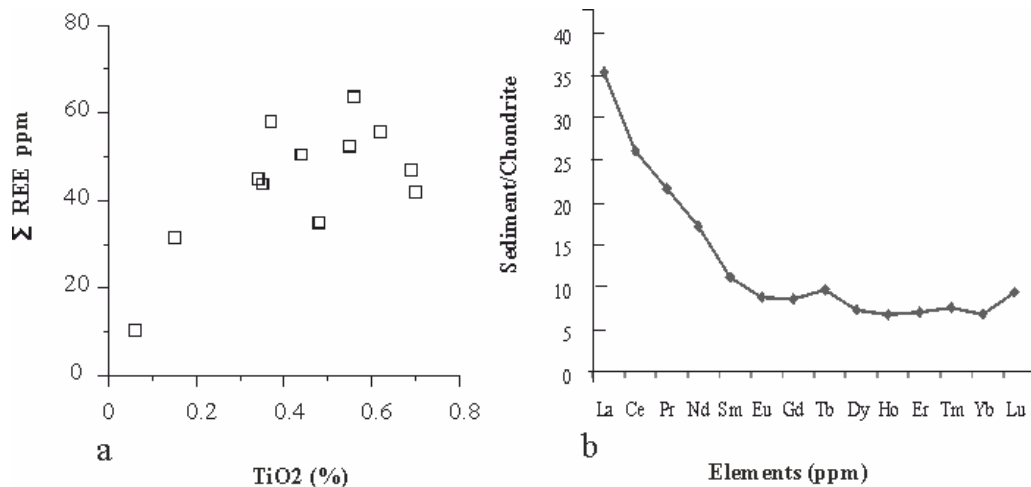
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Figure 10. (a) Correlation graphics between Ti- ∑REE. (b) Chondrite-normalized plot of average REE compositions of lake samples (after McDonough et al. 1992)

4.DISCUSSION

5.1. Origin of the Mg- bearing Minerals

Field observations along with mineralogical paragenesis and the results of geochemical analysis indicate that the studied lake deposits are composed of minerals that were deposited in an alkaline lake environment. Variations in mineralogical and chemical compositions among three sections show that paleogeography played role in lake deposition and, in this respect; different mineral facies are recognized in the study area.

Sepiolite-palygorskite-smectite-calcite-dolomite mineral association was controlled by pH, salinity and/or alkalinity and cation ratios (Si/Al+Fe, Ca/Mg and Mg/H$^+$) and H$_4$SiO$_4$ concentration,. Due to different geomorphologic and hydrologic characteristics of marginal and distal areas, carbonate precipitation increased toward the central areas. Dolomite precipitation took place later on and was very probably related to the different chemistry of the lake water. The dolomitization process was driven by an increase in the Mg/Ca ratio of waters at the center of the lake (Primentel, 2002).

Millot (1964) determined mineralogical changes from the margin of the basin to the lake center in several Tertiary lake basins from northern Africa. According to Millot, (1964), the abundance of Al-bearing materials decreased while that of Mg-silicates increased from the margin of the basin to the lake center. It is also pointed out that if clastic sediment content decreases, a zonation consisting of

smectite-palygorskite, palygorskite-sepiolite develops from margin to the deeper part of the lake. In the lake bain Al-Fe-rich smectites change to Mg-rich clays (palygorskite-sepiolite) from west to east (Fig. 11).
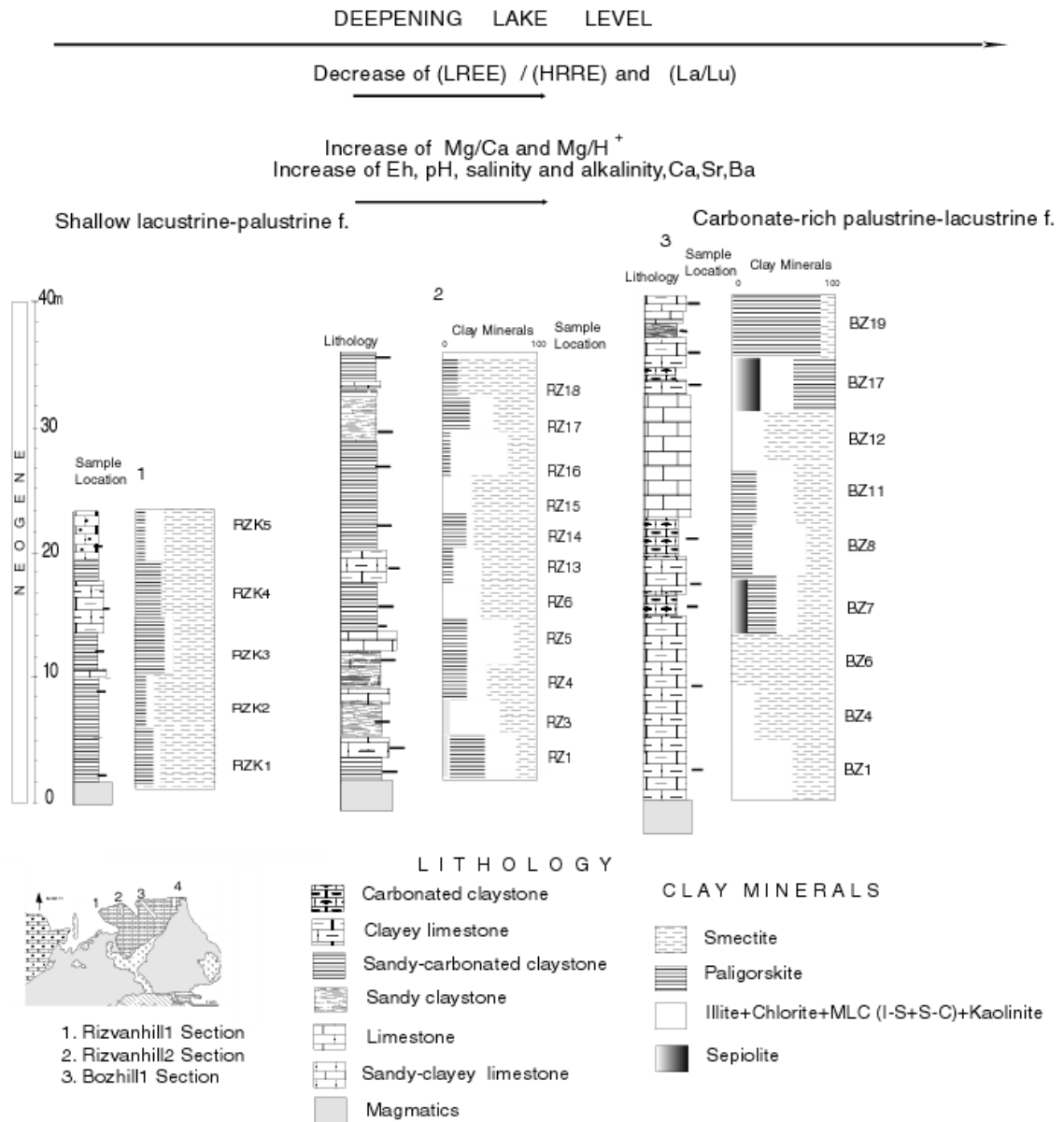

Figure 11. Mineralogic and geochemical variations in two sections of the basin.

Smectite, which is the main clay mineral within the lake basin, might be partly derived from country rocks (Chamley, 1989). Some of the detrital smectite might also be derived from source rocks. Neoformation is also an important mechanism for the precipitation of minerals towards the lake. In other words, the dominance of chemical sediments, particularly in the central parts of the lake, validates the second possibility. The precipitation of smectite from cations released by the rapid hydrolysis of volcanogenic components is a well known mechanism (Boski et al., 1998). The basaltic rocks of Karabakır Formation, represented by the pyroclastic deposits and volcanogenic deposits which outcrop along the eastern margin of the lake basin. In SEM studies, most of smectites have a honeycomb shape (Fig. 5a-b), suggesting an in-situ origin, (Huggenberg & Fuchtbauer, 1988). On the other hand, the spongy texture due to the transformation from volcanic glass, in addition to volcanic glass shards and voids are developed as a result of authigenic smectite formation. Smectites replace volcanic glass, volcanic fragments and rim intergranular pores (Fig. 5a). Likewise, Christidis (2001) described the smectite forming first during dissolution of the volcanic glass through nucleation and crystal growth, leading to pseudomorphic textures and dissolution voids of the volcanic glass.

Elongated crystallites are more typical for Fe-rich smectites (Fig. 5b). The alteration of basic rocks usually yields Fe-rich smectites (Christidis, 2009). Therefore, this type of smectites have neoformation origin and might be formed by the smectitization of Fe-rich mafic minerals or volcanic glass of the Karabakır Volcanics.

Palygorskite in sediments might be formed in various geological environments as detrital, diagenetic or neoformed types (Singer, 1979; Prudêncio et al., 2007). In addition, detrital phyllosilicates and dolomite are also present (Torres-Ruiz et al., 1994; Lopez-Galindo et al., 1996). It is

possible that, like smectite, a small amount of palygorskite could be derived from basement rocks. On the other hand, considering the mineral paragenesis along the lake margin, palygorskite might be also formed by diagenetic transformation of dolomite. Palygorskite is seen as fine and filamentous fibers and coating dolomite (Fig. 5c). These fibrous clay mineral occurrences surrounding carbonate grains are considered to have an authigenic origin by some workers (Hassouba and Shaw, 1980; Estéoule-Choux, 1984). Palygorskite, which is detected almost in all samples, coexisted with calcite, rather than dolomite (Table 1, Fig.5a-b). Palygorskite+calcite must be formed where the Mg/Ca ratio of the environment is low, while palygorskite+dolomite assemblage will be dominant if Mg/Ca ratio is high.

The formation of sepiolite and related minerals in Neogene volcano-sedimentary lake basins was reported by Galan and Castillo (1981) and Starkey and Blackmon (1984). Their works show that the formation of sepiolite is related to basin conditions. For the deposition of sepiolite-bearing thick chemical composition sediments within the central part of the lake basin, Si-, Mg-, Ca- and CO_3-enriched solutions The Mg was supplied from the surrounding, volcanic ash, dolomite and diatomaceous mud act as source materials for sepiolite formation (Fleischer, 1972; Isphording, 1973; Weaver and Beck, 1977; Galan & Ferrero, 1982). Permo-Triassic metacarbonates, middle Eocene-upper Oligocene marine Formation and upper Cretaceous magmatics and Upper Maastrichtian sandstone and recrystalized limestones are suitable source rocks for the formation of sepiolite. The alternation of marly and clayey layers was also possibly a result of periodic climatic changes. Wet periods with materials supplied to the basin favored the formation of palygorskite in Rızvanhill section. During drier periods, evaporitic carbonate and dolomite sedimentation took place, with little sepiolite or smectite formation and a lack of detrital minerals. The eastward decreasing of the palygorskite and

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appearing of sepiolite indicates a basin evolution and perhaps a climate with drier periods in Bozhill section which is deeper part of Lake Basin.

5.2. Element Distribution with Deepening Lake Level

The deepening of the lake basin towards the east, revealed from the distribution of Mg-clays, is also supported by geochemical data.

The arithmetical average of the enrichment factor of Al- and North American shales-normalized elements is computed as $\chi(La/Lu)_{(Nn)(e)}$: $\chi[(La_{sample}/Al_{sample}) / La_{NASC}/Al_{NASC}) / (Lu_{sample}/Al_{sample}) / (Lu_{NASC} / Al_{NASC})]$ (NASC values from Gromet et al. 1984). This ratio is 0.94 for Rızvanhill and 0.44 for Bozhill samples (Table 2). The decrease in this ratio indicates deepening of the basin in such a direction. HREEs are easier to form bicarbonate solution and organic complexes than LREEs in the strong weathering process under warm-humid condition; the HREEs are usually enriched in the solution while LREEs are concentrated in the weathered remnants (Zhang et al., 1997), Therefore, higher LREEs values of Rızvanhill correlated to warmer climate (Tanaka et al., 2007). The scope of paleolake had been expanding and the climate became warm-humid along with the increased paleolake level in Rızvanhill section. Dry climate resulted in narrowing of the lake in Bozhill section which is deeper part of the lake.

5.CONCLUSIONS

The mineralogical and chemical compositions of analyzed samples from lake basin have been used to deduce the following:

1. The mineralogical and geochemical features of the deposit indicate that detritus in the basin fed by from the magmatic-sedimentary and metasedimentary source rocks of the surrounding area. In the lake basin, minerals were formed by transformation of volcanogenic materials.

2. The mineralogy of the lake deposit is mainly composed of clay, calcite, dolomite, quartz, feldspar and opal. Clay minerals are smectite, palygorskite lesser amounts of sepiolite, chlorite, illite, I-S, S-C, and kaolinite.

3. Calcite+smectite+palygorskite mineral association at Rızvanhill section changes to dolomite+smectite+palygorskite+sepiolite assemblage at Bozhill section as a result of the deepening of the lake and an increase in pH, alkalinity and salinity due to deepening of the lake and drier paleoclimate.

4. In SEM studies, most smectites are found to have been formed as space filling by a transformation of volcanic glass or alteration of Fe-rich material in lake water. Volcanic debris is a likely source for smectite because high basaltic levels of Karabakır Formation are found near the lake basin. Some part of smectite and palygorskite must have been derived in detrital form from surrounding rocks however, sepiolite formation is restricted to the deeper part of the basin in Bozhill section which was subjected to drier paleoclimate, and it definitely might be authigenically formed.

5. $\chi(E)_N$ values of SiO_2, Al_2O_3, K_2O, TiO_2, Fe_2O_3, MnO and Ni, Sc, V, Ba, Co, Cs, Ga, Hf, Nb, Rb, Ta, Th, U, Zr ∑REE at Rızvanhill and Bozhill sections are similar show that two section is shallow parts. But Ca is higher Mg and Sr is lower amount in Rızvanhill section may be indicative of shallower parts of the basin, paleolake had been expanding toward Rızvanhill section in warm-humid paleoclimate This is also supported by decreasing $\chi \sum (LREE)_N / \chi \sum (HRRE)_N$ and $\chi (La/Lu)_{Nn(e)}$ values in Bozhill section.

This study has shown that clay mineralogy and the variations of geochemistry might reveal important data on the paleogeography of the paleolake basin and support earlier interpretations.

REFERENCES

Akkoca, D.B., Kalender, L., & Sağıroğlu, A., 2007. *Mineralogy of Neogene lacustrine sediments in the southern vicinity of Elazığ.* Science and Engineering Journal of Fırat University, 19, 3, 363-378.

Aksoy, E., 1993. *General geological properties of west and south of Elazığ.* Turkish Journal of Earth Sciences, TUBITAK, 5, 113-123 (in Turkish whith English abstract).

Alpaslan, M. & Terzioglu, N., 1996. *Comparative geochemical features of the Upper Miocene and Pliocene volcanics in the Arguvan (N - Malatya) area.* Geological Bulletin of Turkey, 39, 2, 75-86.

Aoki S. & Kohyama, N., 1998. *Cenozoic sedimentation and clay mineralogy in the northern part of the Magellan Trough, Central Pacific Basin.* Marine Geolology, 148, 21–37.

Bauluz, B., Mayayo M.J., Fernandez-Nieto C., & López, J.M.G., 2000. *Geochemistry of Precambrian and Paleozoic siliciclastic rocks from the Iberian range (NE Spain): implications for source-area weathering, sorting, provenance, and tectonic setting.* Chemical Geology, 168, 135–150.

Bellanca, A., Di Stefano, E., Di Stefano, P., Erba, E., Neri, R., & Pirini Radrizzani, C., 1993. *Ritrovamento di Calcisfere e nannofossili calcarei in terreni carnici della Sicilia.* Paleopelagos, 3, 91-96.

Bentor, Y.K, 1966. *The Clays of Israel: Guide book to the Excursion, International* Clay Conference, Israel Program for Scientific Translations, pp. 1-121 . Jerusalem.

Boski, T., Pessoa, J., Pedro, P., Thorez, J., Dias, J.M.A., & Hall, I.R., 1998. *Factors governing the abundance of hydrolysable amino acids in the sediments from the NW European continental margin (47–50°N).* Progress in Oceanography, 42, 145–164.

Brindley, G. W., 1980. *Order-disorder in clay mineral structures. In: Brindley G. W. and Brown G. (eds.), Crystal structures of clay minerals and their X-ray identification.* Mineralogical Society, London, 125-195.

Ustillo, M.A., Arribas, M.E., & Bustillo, M., 2002. *Dolomitization and silicification in low-energy lacustrine carbonates (Paleogene, Madrid Basin, Spain).* Sedimentary Geology, 151, 107–126.

Chamley, H.,1989. *Clay sedimentology.* pp. 1-623. Springer Verlag;Berlin.

Chester, R., 1990. *Marine geochemistry*,pp.1-698. Unwin Hyman Press, London.

Christidis, G. E. 2009. *Application of Electron Microscopy to the study of smectites and zeolites.* Revista De La Sociedad Española De Mineralogía, 11, 9-10.

Cullers, R.L., Basu, A., Suttner, L., 1988. *Geochemical signature of provenance in sand-size material in soils and stream sediments near the Tobacco Root batholith, Montana, USA.* Chemical Geology 70(4), 335-348.

Dass Brijraj K. , AL-Mikhlafi A. S, & Kaur P., 2006. *Geochemistry of Mansar Lake sediments, Jammu, India: Implication for source-area weathering, provenance, and tectonic setting. Earth Sciences,* 26, 649-668.

Ercan, T., Fujitani, T., Madsuda, J.I., Notsut, K., Tokel, S., & UI, T., 1990. *Interpretation of new geochemical, radiometric and isotopic data from Neogenen Quaternary volcanics of eastsoutheast Anatolia.* Mineral Research and Exploration Institute (MTA) of Turkey Bulletin, 110**,** 143-164.

Estéoule-Choux, J., 1984. *Palygorskite in the Tertiary deposits of the Armonican masif, in: Occurrences, genesis and uses, Singer A. and Galan, E. (eds.), Palygorskite-sepiolite occurences, genesis, and uses.* Developments in Sedimentology, 37, 59-73.

Fleischer, S.,1972. *Sugars in the sediments of Lake Trummen and reference lakes.* Journal Archiv fur Hydrobiologie, 70, 342- 348.

Galan, E. & Castillo A., 1981. *Sepiolite palygorskite in Spanish Tertiary Basins: Genetical patterns in continental environments.* In: Singer A. and Galan E. (eds.), Palygorskite, Sepiolite, Occurences, Genesis and Uses. Developments in Sedimentology, 87-124.

Gonzalez-Lopez, J.M., Bauluz, B., Fernandez-Nieto, C., & Olite, A.Y., 2005. *Factors controlling the trace-element distribution in fine-grained rocks: the Albian kaolinite-rich deposits of the Oliete Basin (NE Spain).* Chemical Geology, 214, 1–19.

Gromet, L. P., Dymek, R. F., Haskin, L. A., & Korotev, R. L., 1984. *The North American Shale Composite: its compilation, major and trace element characteristics.* Geochimica Cosmochima Acta, 48, 2469– 2482.

Gündoğdu, N. 1982. *Geological-Mıneralogical and Geochemical Investigation of Neogene - Bigadiç Sedimentary Basin.* Hacettepe Üniversity, PhD thesis, pp.1-386.Ankara-Turkey.

Hassan, S., Ishiga, H., Roser, B.P., Dozen, K., & Naka, T., 1999, *Geochemistry of Permian–Triassic shales in the Salt Range, Pakistan: implications for provenance and tectonism at the Gondwana margin.* Chemical Geology, 158 , 293–314.

Hassouba, H. & Shaw. H.F., 1980. *The occurrence of palygorskite in Quaternary sediments of the coastal plain of North-West Egypt.* Clay Minerals, 15, 77-83.

Inglès M, Salvany JM, Munoz A., & Pérez, A., 1998. *Relationship of mineralogy to depositional environments in the nonmarine Tertiary mudstones of the southwestern Ebro Basin (Spain).* Sedimentary Geology, 116, 159-176.

Isphording, W. C., 1973. *Discussion of the occurrence and origin of sedimentary palygorskite-sepiolite deposits.* Clays and Clay Minerals, 21, 391-410.

Johannesson, K. H. & Lyons W. B., 1995. *Rare-earth element geochemistry of Colour Lake, an acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada.* Chemical Geology, 119, 209–223.

Jones, B. F., 1986. *Clay mineral diagenesis in lacustrine sediments.* In: F. A., Mumpton (eds.), Studies in Diagenesis. U. S. Geological Survey Bulletin, 1578, 291-300.

Kelts, K. &Hsu, K., 1978. *Freshwater carbonate sedimentation.* In: Lerman A. (eds.), Lakes—chemistry, geology, physics, pp. 295–323, Springer, New York,

Kürüm, S., Akgül, B., & Erdem, E., 2006. *Examples of Neogene Volcanism in Eastern Turkey: comparative petrographic, geochemical and petrologic features of Malatya-Elazığ-Tunceli Volcanics.* Journal Geological Society of India, 68, 129-136.

Leo,D.P., Dinelli, E., Mongelli, G., & Schiattarella, M., 2002. *Geology and geochemistry of Jurassic pelagic sediments, Scisti Silicei Formation, southern Apennines, Italy.* Sedimentary Geology, 150, 229-246.

Lepane, V., Varvas, M., Viitak, A., Alliksaar, T. & Heinsalu, A. 2007. *Sedimentary record of heavy metals in Lake Rıuge Liinrv, southern Estonia.* Estonian J. Earth Sci., 56, 221-232.

Lopez-Galindo, A., Ben Aboud, A., Fenoll Hach-Ali, P., & Casas Ruiz, J., 1996. *Mineralogical and geochemical characterization of palygorskite from Gabasa (NE Spain); evidence of a detrital precursor.* Clay Minerals, 31, 33-44.

McDonough, W.F., Sun, S.-S., Ringwood, A.E., Jagoutz, E., & Hofmann, A.W. 1992. *Potassium, Rubidium and Cesium in the Earth and Moon and the evolution of the mantle of the Earth.* Geochimica et Cosmochimica Acta 56, 1001-1012.

McLennan, S.M., 1989. *Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes*, In: Lipin B.R.., McKay G.A. (eds.), Geochemistry and Mineralogy of Rare Earth Elements. Mineralogical Society of America Reviews in Mineralogy**,** 169-200.

McLennan, S.M. & Taylor S.R., 1991. *Sedimentary rocks and crustal evolution: Tectonic setting and secular trends.* Journal of Geology, 99, 1-21.

Millot, G., 1964, Gdologie des Argiles,pp. 1- 425 .Masson et Cie, Paris.

Möller P. & Bau M., 1993. *Rare-earth patterns with positive cerium anomaly in alkaline waters from Lake Van Turkey.* Earth and Planetary Science Letters, 117**,** 671–676.

Plank, T. & Langmuir, C. H., 1998. *The chemical composition of subducting sediment and its consequences for the crust and mantle.* Chemical Geology, 3, 325-394 .

Primentel, N. L. V., 2002. *Pedogenic and early diagenetic processes in Palaeogene alluvial fan and lacustrine deposits from the Sado Basin (S Portugal).* Sedimentary Geology, 148, 123-138.

Prudêncio, M. I., Gonzalez, M. I., Dias, M. I., Galan, E., & Ruiz, F., 2007. *Geochemistry of sediments from El Melah lagoon (NE Tunisia): A contribution for the evaluation of anthropogenic inputs.* Journal of Arid Environments, 69, 285–298.

Reeves H.M, Dill H.H., & Hawkins, A.S., 1968, *A case study in Canada goose management: the Missisipi Valley population* (in): Hine R.L. and Schoenfeld, C. (eds.), Canada Goose Management. pp.1-195. Dembar Education Research Services, Madison.

Roy, P. D. &Smykatz-Kloss, W., 2007. *REE geochemistry of the recent playa sediments from the Thar Desert, India: An implication to playa sediment provenance*. Chemie der Erde, Geochemistry, 67, 55-68.

Saez, A., Anado´n, P., Herrero, M.J., & Moscariello, A. 2007. *Variable styles of transition between Palaeogene fluvial fan and lacustrine systems, southern Pyrenean foreland, NE Spain.* Sedimentology, 54, 367–390.

Shoval, S., 2004. *Clay sedimentation along the southeastern Neo-Tethys margin during the oceanic convergence stage.* Applied Clay Science, 24 , 287–298.

Singer, A., 1979. *Palygorskite in sediments: detrital, diagenetic or neoformed, A critical review. Geoliche Rundschau,* 68, 996-1008.

Starkey, H.C. & Blackmon, P.D., 1984. *Sepiolite in Pleistocene Lake Tecopa, Inyo Country, California. In: Singer, E., Galán, E. (eds.), Palygorskite–sepiolite: occurance, genesis and uses.* Development in Sedimentology, 37, 137-147.

Şengör C. & Yılmaz, F., 1981. *Tethyan evolution of Turkey: a plate tectonic approach.* Tectonophysics, 75**,** 181–241.

Talbot, M.R., 1990. *A review of the paleohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates.* Chemical Geology (Isotope Geoscience Section), 80, 261-79.

Talbot, M.R. & Kelts, K., 1990. *Paleolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic carbon - rich lacustrine sediments. In: Katz, B., (eds.), Lacustrine Basin Exploration: Case Studies and Modern Analogs.* American Association of Petroleum Geologists Memoir, 50, p.99-112.

Tanaka K, Akagawab F, Yamamoto K, Tani Y., Iwao K., Kawai T., 2007. *Rare earth element geochemistry of Lake Baikal sediment: Its implication for geochemical response to climate change during the Last Glacial/Interglacial transition.* Quat Sci Rev, , 26: 1362 ─ 1368.

Taylor, S. R. & McLennan, S. H., 1985. *The Continental Crust: Its Composition and Evolution,*pp. 1-312 , Blackwell, Oxford.

Tlili, A., Felhi, M., & Montacer, M., 2010. *Origin and depositional environment of paligorskite and sepiolite from the Ypresian phosphatic series, sothwestern Tunisia. Clays and Clay Minerals,* 58, 4, 573-584.

Torres-Ruiz J., Lopez-Galindo A., Gonzales-Lopez, J.M., & Delgado, A., 1994. *Geochemistry of Spanish sepiolite-palygorskite deposits: Genetic considerations based on trace elements and isotopes.* Chemical Geology, 12 , 221–245.

Üstündag, S., 1996, *Petrographic Properties of Limestones of Karabakır Formation around Elazığ, Master thesis, Firat University Graduate School of Natural and Applied Sciences*, pp. 1-39, Elazıg, Turkey.

Volkova, N.I., 1998. *Geochemistry of rare elements in waters and sediments of alkaline lakes in the Sasykkul depression, East Pamirs.* Chemical Geology, 147, 265-277.

Weaver, C.E. & Pollard, L.D., 1973. *The Chemistry of Clay Minerals: Developments in Sedimentology,* pp. 1- 213 .Elsevier Scientific Publishing, Amsterdam,

Weaver, C. E. & Beck, K. C., 1977. *Miocene of the S.E. United States: A Model for Chemical Sedimentation in a Peri-marine Environment*. Sedimentary Geology, 17, 201-225.

Worash G. & Valera, R., 2002, *Rare earth element geochemistry of the Antalo Supersequence in the Mekele Outlier (Tigray region, northern Ethiopia).* Chemical Geology, 182, 395-407.

Yalçın, H. & Bozkaya Ö., 2002, *Alteration mineralogy and geochemistry of the Upper Cretaceous Volcanics around Hekimhan (Malatya), central east Turkey: An sample for the seawater-rock interaction.* Bulletin of Faculty of Engineering of Cumhuriyet University, 19/1, 81-98.

Galan I. & Ferrero A., 1982. *Palygorskite - sepiolite clays of Lebrija, southern spain E.*, Clays and clay minerals, 30, 3,191-199.

Zhang H. C., 1998. *The REE of Wuwei loess at south vicinity of Tengger Desert and a model for loess accumulation (in Chinese with English abstract).* J Lanzhou Univ (Nat Sci Ed), , 34(4): 157—164.