

First data on the geochemistry of fluvial deposits of Çaybağı and Palu formations (Eastern Elazığ, Turkey)

Çaybağı ve Palu formasyonu akarsu yataklarının jeokimyasına ait ilk bulgular (Elazığ'ın Doğusu, Türkiye)

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Geliş Tarihi/Received: 20.02.2017, Kabul Tarihi/Accepted: 14.09.2017
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doi: 10.5505/pajes.2017.25665
Araştırma Makalesi/Research Article

Abstract

In this study, the geochemistry (major, trace and rare earth elements) of fluvial deposits of the Çaybağı and Palu Formations, Eastern Elazığ, have been investigated. The basement of the studied basin is composed of the Guleman Group, Elazığ Magmatics, Hazar-Maden Group, and Kırkgeçit Formation which consist of volcanic materials derived from the Elazığ Magmatics. The Çaybağı Formation is composed of thick fluvio-lacustrine sedimentary sequence. Palu Formation consists of alluvial fan deposits and braided river, lacustrine sedimentary deposits. Samples were collected from braided river deposits of Çaybağı and Palu Formation along Hacısamdere-Çaybağı section (Ç-samples) and Hacısamdere-Palu section (PL samples). Significant positive correlation between Zr/Sc and Th/Sc ratios of two sample groups show that the siliciclastic sample groups do not represent considerable sediment recycling. Çaybağı and Palu samples have similar geochemical indices (Al_2O_3/TiO_2 , Ti/Zr , La/Th , La/Sc , Cr/Th , Co/Th , $(La/Yb)_N$, $(Gd/Yb)_N$, LREE/HREE ratios) and indicate derivation from intermediate-basic source rocks. In Si vs. Na/K diagram samples plot in arc field and La/Sc and Ti/Zr ratios show that samples were plotted in an oceanic island arc environment.

Keywords: Elazığ, Fluvial deposits, Geochemistry, Tectonic setting

Öz

Bu çalışmada Elazığ'ın doğusundaki Çaybağı ve Palu Formasyonu'na ait fluvial çökellerin jeokimyası (majör, iz ve nadir toprak elementler) incelenmiştir. İnceleme alanının temel kayalarını Guleman Grubu, Elazığ Magmatitleri, Hazar-Maden Grubu, Elazığ Magmatit'lerinden malzeme almış olan Kırkgeçit Formasyonu oluşturmaktadır. Çaybağı Formasyonu kalın fluvial-lakustrin sedimanter istiften, Palu Formasyonu alüvyon yelpazesi, örgülü nehir çökelleri, lakustrin sedimanlardan oluşmaktadır. Örnekler Hacısamdere-Çaybağı kesiti (Ç örnekleri) ve Hacısamdere-Palu kesiti (PL örnekleri) boyunca Çaybağı ve Palu Formasyonları'nın nehir çökellerinden alınmıştır. Zr/Sc ve Th/Sc oranı arasında önemli pozitif korelasyonun görülmesi örneklerin önemli bir sedimanter çevrime maruz kalmadığını göstermektedir. Çaybağı ve Palu örneklerinin benzer jeokimyasal indisleri (Al_2O_3/TiO_2 , Ti/Zr , La/Th , La/Sc , Cr/Th , Co/Th , $(La/Yb)_N$, $(Gd/Yb)_N$, LREE/HREE oranları), bunların nötr-bazik kaynak kayalarından türediğini göstermektedir., Si'a karşı Na/K diyagramında örnekler yay alanına düşmektedir. La/Sc, Ti/Zr oranları örneklerin okyanus adayayı ortamında depolanmış kayalardan türediğini göstermektedir.

Anahtar Kelimeler: Elazığ, Akarsu yatakları, Jeokimya, Tektonik ortam

1 Introduction

The geochemical composition of clastic rocks is widely used to understand the composition [1],[2] and evaluate weathering processes [3]-[5], and investigate the depositional setting and its associated provenance [6]-[13]. The compositions of sedimentary rocks depend on their source rocks, the geochemistry of sedimentary rocks and their provenance has been investigated by many workers [14- 20]. TiO_2 , La, Y, Sc, Cr, Th, Zr, Hf, Nb, and rare earth elements (REE) are very suitable for provenance studies [21].

During the Neogene to Quaternary various lacustrine and fluvial deposits (e.g. The Çaybağı and Palu Formations) were accumulated in Eastern Turkey (Figure 1a). These deposits consist of sandstone, siltstone, and carbonaceous claystones. Perinçek and Özkaya, Özkul, Sungurlu et al., Çetindağ [22-25] studied the geological, hydrological, sedimentological characteristic of the study area. The depositional environment of the Çaybağı Formation is studied in detail by [26],[27] described five types of facies associations in the Çaybağı Formations; braided river, low-sinuosity river, lacustrine delta front, lacustrine shallow and open lacustrine environments. Mineralogical variations and authigenic mineral occurrences

in the Çaybağı Formation were studied by Akkoca and Sağroğlu [28]. Palu Formation was named and studied by [25],[29] investigated sedimentological characteristics of Palu Formation and they defined alluvial fan deposits and braided river deposits in the formation. Çolak et al. [30] mentioned lacustrine environment within the formation. In spite of these geological, sedimentological and mineralogical investigations, the geochemistry of these two formations has not been studied. Therefore the purpose of this paper is to evaluate the river deposits of Çaybağı and Palu Formations, in order to provide information on the provenance of detrital material, and to constrain tectonic setting of the sediments from these formations.

2 Geology

The study area is located in the eastern part of Elazığ city (Figure 1a). The basement of the studied Çaybağı and Palu Formations is composed of Jurassic-Upper Cretaceous Guleman Ophiolites, Upper Cretaceous Elazığ Magmatics, Upper Maastrichtian-Middle Eocene Hazar Group, Middle Eocene Maden Group and Middle Eocene-Lower Oligocene Kırkgeçit Formation (Figure 1b).

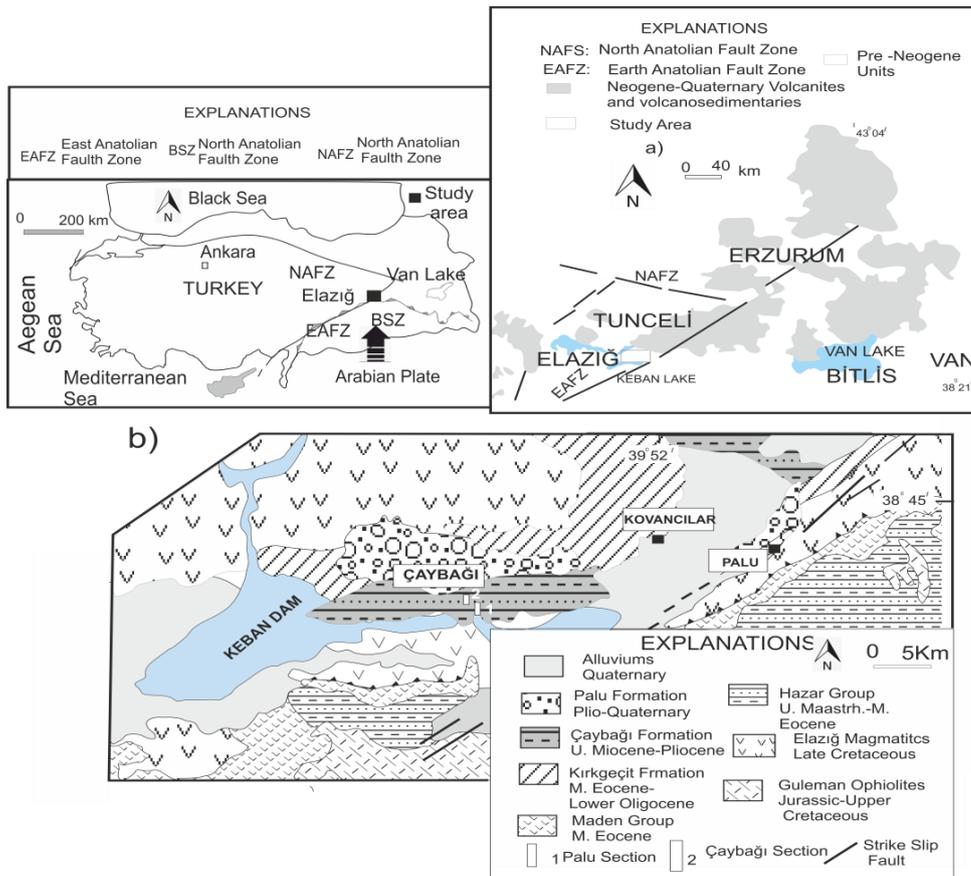


Figure 1: (a): Distribution of the Neogene-Quaternary units in eastern Turkey (after Koç Taşgın and Türkmen [27]).
(b): Detailed geological map of the study area (modified from Çelik[40]).

The Guleman Ophiolite consists of ultramafic sequence including dunite, harzburgite with podiform chromite, alternating dunite-wehrlite-clinopyroxenite banded gabbro, quartz gabbro/diorite and volcanites.

Yazgan and Chessex [31] suggest that the ophiolites are formed around 85-76 Ma, based on K-Ar dating of biotite separates and whole-rocks [32]. Dönmez [33] studied the Upper Cretaceous Elazığ Magmatites around the Soğanlı and Uyandık Villages of the Kovancılar Country. They determined that magmatic succession includes basaltic pillow lavas, pyroxene-bearing andesitic lava flows, and pyroclastics volcanogenic sandstones. Geochemical data indicate that the Elazığ Magmatites consists of a calc-alkaline series and that they are the products of island-arc magmatism [31],[33]-[35]. These magmatic rocks are overlain by limestone, sandstone, and marls of the Kırkgeçit Formation, which was deposited in variable shallow to relatively deep-marine Middle Eocene-Lower Oligocene clastic sediments [36]. This formation is fed from Elazığ Magmatites and contains pebbles of magmatites exposing around the study area.

The Maden Group consists of limestones, red-green clayey limestones, sandstone and agglomerate, tuffs, reddish mudstone and basaltic-andesitic pillow lavas. There are several suggestions on the origin of Group. The Maden Group is a volcanosedimentary succession of Middle Eocene age representing a short-lived back-arc basin which reached the stage of an embryonic ocean [37]. The basaltic-andesitic rocks

of Group would be possibly have formed by rifting of the fore-arc, probably related to oblique convergence in the Middle Eocene [38]. The Maden Group which conformably covers the Hazar Group was formed in an E-W trending extensional basin in the Middle Eocene. Hazar Group consists of conglomerates that are laterally and vertically in transition with limestone consisting of sandy limestone and grey-brown shales. Çelik [39] suggests that this formation was deposited in shallow parts of the Hazar-Maden Basin.

The Çaybağı Formation, which was named by Türkmen [41], was later studied in much detail by Koç Taşgın and Türkmen [42] for stratigraphical and sedimentological characteristics. The Çaybağı Formation unconformably overlies the Kırkgeçit Formation at north and east and Elazığ Magmatites at west (Türkmen 1991). It comprises a thick (~ 1987 m) alluvial fan, delta, fluvio-lacustrine sedimentary sequence made up of numerous lithofacies.

According to Koç Taşgın and Türkmen [42], the Çaybağı Formation was deposited in a variety of environments which are from bottom to top, the Hacısamdere, the Yılkaya, the Ziyarettepe and the Arılar members. Koç Taşgın and Türkmen [42] states that Hacısamdere member, from which samples were collected, is fining-upward and was deposited by a fluvial system. Fluvial deposits of the formation consist of a matrix-supported conglomerate, tuff, sandstone, and red-grey clayey sandstone, limestone and claystone alternation (Figure 2a). Pebbles in the conglomerates are derived from the

Elazığ Magmatics and Kırkgeçit Formation. The measured thickness of this member is about 350 m. Koç Taşgın and Türkmen [27] suggest that this sequence is composed of typical braided river deposits which directly fed lacustrine environment (Figure 2b). Based on fossil content the age of formation was suggested as Upper Miocene-Pliocene [42].

Palu Formation was first recognized and named by Çetindağ [25] in the Palu County. Formation is well-exposed along the northeastern margin of the Palu-Uluova basin, particularly in the west of Palu County. It consists mainly of braided river, fan delta, fluvial coarse clastics with fine-grained lacustrine sedimentary intercalations [30]. Alluvial fan deposits are formed by conglomerates and pebbly sandstones (Figure 2(c)). Pebbles are partly well- to sub-rounded and partly angular clasts of mostly magmatic rocks such as andesite, basalt, sandstone and limestones and derived from the Elazığ Magmatics and Kırkgeçit Formation. Braided river deposits mainly composed of conglomerates, volcanogenic sandstone, and cross-bedded clayey sandstones (Figure 2(d)). Volcanogenic sandstone consists of unsorted, weakly lithified and matrix-supported pebbles and blocks (up to 1 m in diameter) of conglomerates and is partly well to sub-rounded and partly angular clasts of mostly magmatic rocks such as andesite, basalt, sandstone and limestones and derived from the Elazığ Magmatics. Kerey and Türkmen [29] suggest that transportation direction of alluvial fans is from north to south and that of braided rivers is from east to the west.

3 Material and methods

Eighteen sandstone samples were collected from braided river deposits of Çaybağı and Palu Formation along Hacısamdere-Çaybağı section (Ç samples, river facies from Hacısamdere

member) and Hacısamdere- Palu section (PL samples, braided river facies) (Figs. 1 and 3).

Chemical analyses of representative samples were conducted at Acme Analytical Laboratories Ltd. (Canada). Trace element and major oxide compositions of samples were determined by ICP-AES and REEs were analyzed by ICP-MS. Major, trace and rare earth elements were measured ICP-ES and ICP-MS techniques on glass pellets which were produced in platinum-gold crucible adding 1/5 ratio of sample and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) at 1150 °C. Correlation coefficients were calculated from the data set for geochemical analyses. Accordingly, the significance level is $\alpha = 0.05$.

4 Results and interpretations

4.1 Geochemistry

4.1.1 Major and trace element geochemistry

Major and trace element concentrations, average (\bar{x}), standard deviations (St.D.) of the analyzed samples are given in Table 1-2. The average data of Post-Archean Australian shales (PAAS) which represent the felsic upper continental crust composition are taken as reference.

In Çaybağı and Palu samples, average concentrations of SiO_2 , Al_2O_3 , Fe_2O_3 and MgO are 46.91 % and 53.98%, 13.21 % and 14.42%, 7.96% and 8.27% and 5.21% and 3.90%. Major element values of two sample groups are not close to PAAS since the source rock of studied samples has intermediate-basic character. For these reason, Fe_2O_3 , CaO , MgO , and Cr_2O_3 contents are higher, SiO_2 , Al_2O_3 , K_2O contents are lower than PAAS (Figure 4(a)). In the [43] diagram, samples of two groups are defined as "Fe-sand" (Figure 4(b)).

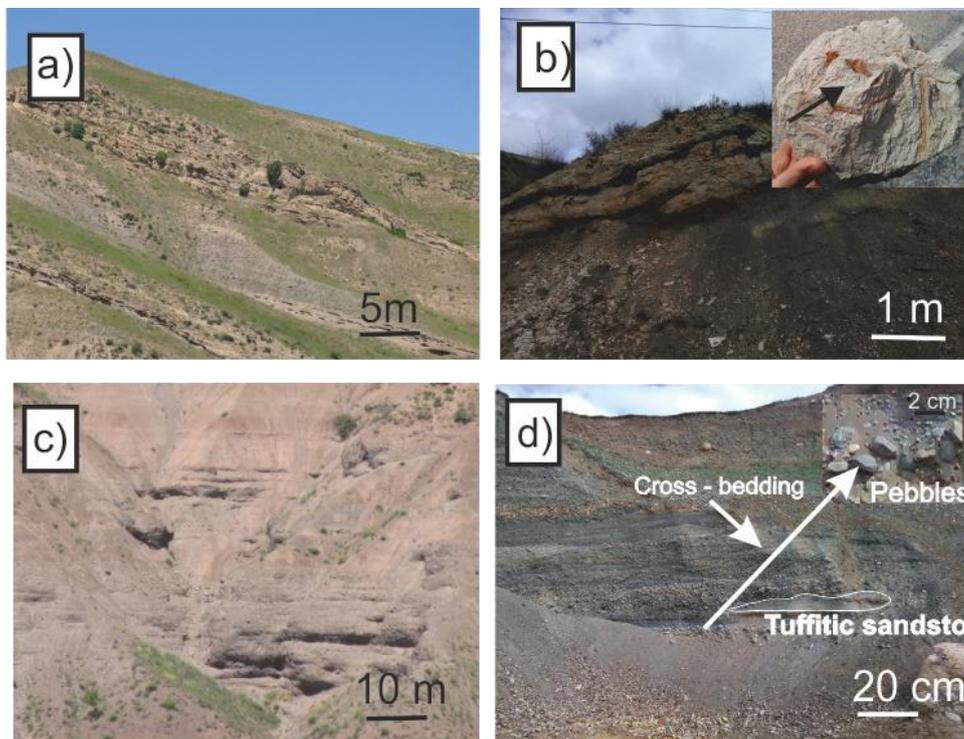


Figure 2: (a): The fluvial deposits of Çaybağı Formation (5 km SE of Çaybağı village, view to NW). (b): Thick carbonated rock layer of lacustrine sedimentary sequences from Çaybağı Formation (leaf fossils could be see). (5.5 km NE of Çaybağı village, view to E). (c): Fan delta and alluvial fan deposits from Palu Formation 4 km E of Çaybağı village, view to W. (d): Braided river of Palu Formation). (4 km NE of Çaybağı village, view to E).

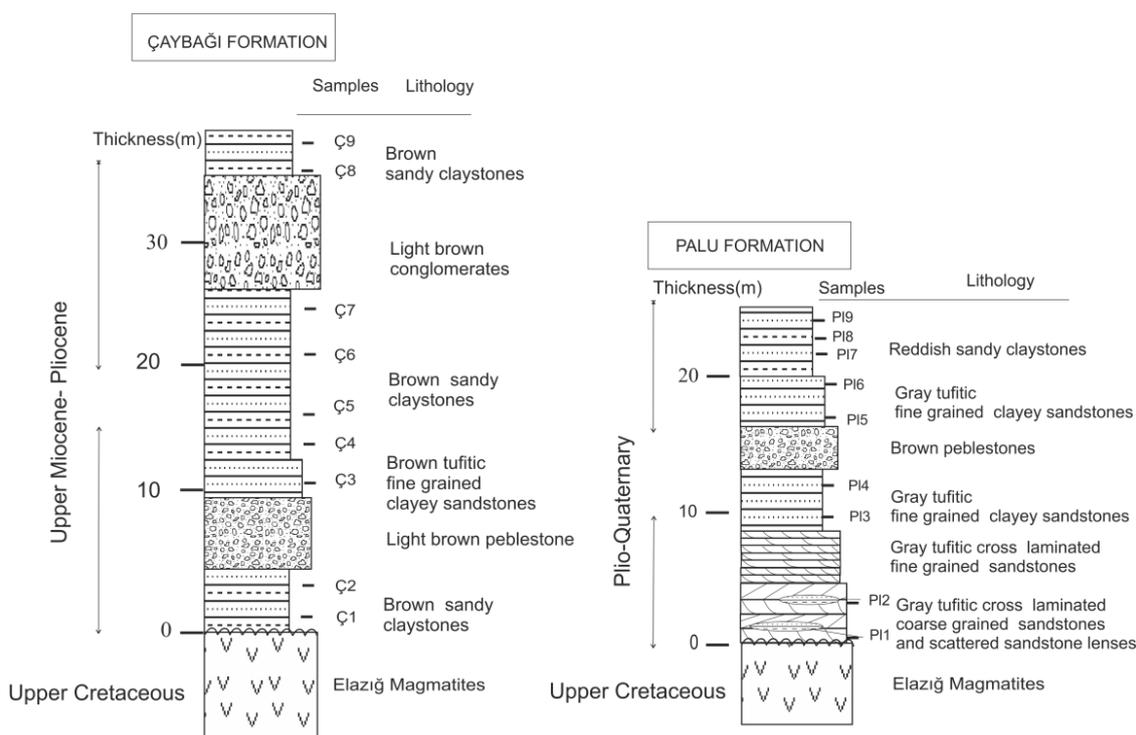


Figure 3: Measured lithostratigraphic section of Hacısamdere-Çaybağı and Hacısamdere-Palu, showing the location of samples.

Table 1: Major and trace elemental abundances of Çaybağı (Ç) and Palu (PL) samples and Average Post-Archean Australian shale. PAAS; data from Taylor and Mc Lennan [44] for comparison.

Sample	Concentration (wt.%)												LOI
	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	Al ₂ O ₃ / TiO ₂	
Ç1	53.03	14.25	8.40	4.01	9.06	2.87	0.55	1.08	0.14	0.15	0.026	11.03	6.3
Ç2	53.93	14.77	8.41	4.47	6.64	2.78	0.82	1.06	0.16	0.14	0.030	12.67	6.6
Ç3	46.23	13.10	8.11	5.42	8.26	1.19	1.09	0.81	0.09	0.11	0.063	13.21	15.3
Ç4	47.91	13.26	7.85	5.37	8.21	1.52	0.98	0.84	0.09	0.13	0.060	12.59	13.6
Ç5	41.07	11.72	7.21	4.66	13.90	1.35	0.87	0.76	0.10	0.26	0.073	12.38	17.8
Ç6	44.94	12.94	7.81	5.25	10.01	1.49	0.97	0.82	0.10	0.15	0.072	17.05	15.2
Ç8	43.02	13.19	9.04	6.51	8.31	0.90	0.98	0.75	0.11	0.13	0.047	15.74	16.8
Ç9	45.00	12.55	7.41	5.17	10.29	1.28	1.04	0.79	0.10	0.12	0.068	13.92	16.0
Ç10	47.10	13.15	7.37	6.03	8.82	1.84	0.89	0.92	0.10	0.09	0.073	14.21	13.4
Average	46.91	13.21	7.96	5.21	9.28	1.69	0.91	0.87	0.11	0.14	0.06	13.43	13.44
St. Dev.	3.60	0.80	0.57	0.63	2.04	0.53	0.09	0.10	0.02	0.05	0.01	2.11	3.25
PL1	57.03	14.45	8.81	3.26	6.81	3.42	0.66	1.31	0.16	0.14	0.037	13.19	3.7
PL2	54.51	14.58	8.30	3.91	7.64	3.20	0.73	1.15	0.15	0.12	0.035	13.93	5.5
PL4	56.23	15.06	8.56	4.02	7.16	3.24	0.49	1.14	0.16	0.16	0.031	16.17	3.6
PL5	54.80	15.24	9.06	4.17	7.33	3.42	0.57	1.21	0.18	0.14	0.029	15.78	3.7
PL7	54.76	13.61	7.37	3.60	7.11	3.03	1.16	1.31	0.16	0.23	0.078	15.42	7.4
PL8	56.08	15.35	8.71	4.15	5.99	2.74	0.64	0.90	0.16	0.13	0.023	15.78	4.9
PL9	55.59	15.43	8.17	4.28	5.76	2.90	0.68	0.98	0.17	0.14	0.029	17.58	5.7
PL10	44.38	12.53	7.26	3.78	11.95	1.57	0.90	0.90	0.10	0.14	0.039	15.88	16.3
PL11	52.40	13.50	8.23	3.96	8.55	3.16	0.38	0.95	0.10	0.13	0.022	14.29	8.4
Average	53.98	14.42	8.27	3.90	7.59	2.96	0.69	1.09	0.15	0.15	0.04	15.34	6.58
St. Dev.	3.83	1.00	0.62	0.32	1.83	0.57	0.23	0.17	0.03	0.03	0.02	1.08	4.01
PAAS	62.8	18.9	6.5	2.2	1.3	1.2	3.7	1	0.16	0.11	0.007	18.9	0.007

Table 1'in continued.

Table 1. Continued		Concentration (ppm)									
Sample	Co	Cs	Ga	Hf	Nb	Rb	Sr	Ta	Th	U	V
Ç1	22.7	0.7	15.1	2.6	4.3	15.2	184.7	0.3	1.9	0.5	240
Ç2	23.2	0.9	13.6	3.6	6.9	22.1	214.3	0.5	3	0.9	211
Ç3	31.5	1.8	12.1	2.2	7.2	30.6	200.5	0.5	3.1	1	175
Ç4	35	1.4	11.7	2	5.9	23.4	238.2	0.3	2.3	0.8	195
Ç5	27.2	1.1	9.6	2	5.4	21	235.2	0.3	1.9	0.7	166
Ç6	31.7	1.1	10.9	2	5.6	23.4	232.2	0.3	2.5	0.7	191
Ç8	33.5	1.5	11.7	2.1	6.2	26.9	195.3	0.4	2.7	0.7	177
Ç9	30	1.3	10	2	6	25.9	202.6	0.4	2.4	0.8	178
Ç10	31.5	0.6	11.1	1.8	5	17.8	247.1	0.3	1.8	0.5	198
Average	29.6	1.2	11.8	2.3	5.8	22.9	216.7	0.4	2.4	0.7	192.3
St. Dev.	4.089	0.365	1.619	0.519	0.847	4.401	20.864	0.082	0.45	0.156	21.333
PL1	19	0.9	15.7	3.4	6	17.2	269.1	0.4	2.8	0.7	250
PL2	21.1	0.8	15.2	3.2	6.3	19.3	309	0.4	2.8	1.3	233
PL4	20.7	0.4	14.5	3	4.1	11.3	214	0.3	1.8	0.4	236
PL5	25.1	0.4	14.7	2.8	4.4	12.1	239.8	0.3	2.9	0.5	261
PL7	22.6	1.5	14	5	10.8	31.2	327.1	0.8	4.7	1.7	181
PL8	21.7	0.6	14.1	2.4	4	15.7	194	0.3	2.3	0.6	234
PL9	24.1	0.8	14.7	2.8	4.6	16.8	214	0.3	2.5	0.7	202
PL10	24.9	1.8	12.3	3.2	7.9	28.9	197.4	0.4	3.6	1	179
PL11	24.6	0.2	11.9	1.9	1.8	7.8	222.8	0.1	0.7	0.5	267
Average	22.6	0.8	14.1	3.1	5.5	17.8	243	0.4	2.7	0.8	227
St. Dev.	2.04	0.5	1.19	0.81	2.46	7.34	45.57	0.18	1.05	0.41	30.72
PAAS	23	15	20	5	19	160	200	---	14	3.1	150

Table 1. Continued

Table 1. Continued		Concentration (ppm)								
Sample	Zr	Y	Mo	Cu	Pb	Zn	Sc	As	Ba	Ni
Ç1	102.7	21.9	0.2	34.2	4.4	49	26	2.5	131	66
Ç2	151.9	28.5	0.2	31.2	5.4	49	26	3.3	135	67
Ç3	86	19.1	0.1	56.2	6.9	71	24	1.4	138	196
Ç4	77.9	18.8	0.1	55.5	5.3	65	26	1.3	138	187
Ç5	75.3	21.3	0.1	49.9	5	65	23	1.5	126	155
Ç6	80.2	20.5	0.1	55.4	5.8	67	25	2	139	184
Ç8	80.9	16.8	0.1	59.6	6.1	85	25	2	114	206
Ç9	80.8	19.8	0.2	60.2	6.1	70	24	1.9	144	190
Ç10	72.5	17.2	0.1	52.2	4	63	27	1.8	101	195
Average	89.8	20.4	0.1	50.5	5.4	64.9	25.1	2	129.6	160.7
St. Dev.	23.43	3.274	0.047	9.999	0.85	10.44	1.197	0.585	13.09	52.013
PL1	128.7	26.1	0.3	25.7	2.3	49	22	2.9	152	46
PL2	120	42.8	0.3	28	3.1	55	23	2.2	179	66
PL4	110.9	28.3	0.3	34	5.5	55	26	2.6	99	57
PL5	107.7	25.4	0.3	39.3	5.6	54	27	2.3	128	58
PL7	203.6	24.5	0.2	18.6	5.2	47	19	3.1	288	105
PL8	94.8	22.4	0.2	33.5	5.9	64	25	4.1	105	59
PL9	107.9	24.7	0.2	32.1	5.3	58	25	2.6	136	78
PL10	117.1	21.3	0.2	31.1	7.1	71	20	4.5	201	104
PL11	67.7	20.7	0.2	27.9	4.2	70	25	3.4	93	54
Average	117.6	26.2	0.2	30	4.9	58.1	23.6	3.1	153.4	69.7
St. Dev.	34.6	6.28	0.05	5.55	1.39	8.06	2.59	0.75	58.63	20.35
PAAS	210	30	---	50	20	85	16	---	650	55

Table 2: Rare earth element concentrations (ppm) of Çaybağı and Palu samples and Post-Archean Australian shale (PAAS) for comparison. $Eu/Eu^* = (Eu)_N / [(Sm)_N](Gd)_N]$. N: Chondrite normalization values are from [52].

Table 2		Concentration (ppm)								
Samples	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	
C1	10	20	2.82	12.5	3.01	1.04	3.53	0.65	4.09	
C2	14.5	27.5	3.95	17	4.04	1.1	4.65	0.81	4.88	
C3	12.7	24.9	3.28	13.2	2.91	0.87	3.41	0.57	3.58	
C4	10.3	20.6	2.65	11.4	2.83	0.89	3.29	0.55	3.3	
C5	11.8	21.5	2.95	12.8	2.85	0.85	3.38	0.54	3.72	
C6	11.8	21.6	2.98	12.4	2.89	0.94	3.44	0.56	3.54	
C8	10.7	21.2	2.76	11.7	2.92	0.8	3.04	0.52	3.22	
C9	11.7	24.3	2.98	12.4	2.85	0.85	3.18	0.57	3.45	
C10	8.1	16.9	2.23	10.4	2.49	0.8	2.92	0.5	3.12	
Average	11.3	22.1	3	12.6	3	0.9	3.4	0.6	3.7	
St. Dev.	1.7	2.92	0.44	1.73	0.4	0.1	0.47	0.09	0.51	

Table 2: Continued.

Concentration (ppm)									
Samples	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
PL1	12.8	27.5	3.56	15	3.64	1.16	4.33	0.76	5.14
PL2	12.7	24.9	3.33	14.5	3.52	1.09	4.71	0.86	6.04
PL4	9	20.8	2.83	13.6	3.49	1.17	4.34	0.77	4.64
PL5	9.2	20.8	2.9	12.7	3.49	1.21	4.03	0.69	4.41
PL7	17.8	37.2	4.49	17.5	3.93	1.17	4.34	0.7	4.33
PL8	8.3	19.1	2.45	11.1	2.8	0.93	3.39	0.62	3.85
PL9	11.8	25.3	3.21	14.2	3.29	1.07	4.1	0.69	4.35
PL10	14.7	30.7	3.73	15.4	3.65	0.99	3.91	0.63	4.05
PL11	6	12.7	1.87	8.9	2.48	0.94	3.19	0.57	3.48
Average	11.4	24.3	3.2	13.7	3.4	1.1	4	0.7	4.5
St. Dev.	3.24	6.36	0.68	2.25	0.4	0.09	0.43	0.08	0.67
PAAS	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68

Concentration (ppm)									
Samples	Ho	Er	Tm	Yb	Lu	(La/Yb) _N	(Gd/Yb) _N	Eu/Eu*	
C1	0.84	2.45	0.33	2.34	0.37	3.16	1.25	0.95	
C2	1.01	3	0.42	2.84	0.41	3.77	1.35	0.76	
C3	0.73	2.05	0.3	2.11	0.3	4.45	1.34	0.82	
C4	0.72	2.08	0.29	1.98	0.3	3.84	1.37	0.87	
C5	0.72	2.15	0.3	2.01	0.31	4.34	1.39	0.82	
C6	0.75	2.19	0.33	2.03	0.31	4.3	1.4	0.89	
C8	0.68	2.03	0.28	1.82	0.29	4.35	1.38	0.8	
C9	0.67	1.95	0.29	1.85	0.28	4.67	1.42	0.84	
C10	0.65	1.88	0.27	1.86	0.27	3.22	1.3	0.89	
Average	0.8	2.2	0.3	2.1	0.3	4	1.4	0.8	
St. Dev.	0.1	0.32	0.04	0.3	0.04	0.51	0.05	0.05	

PL1	1.01	3.07	0.44	2.89	0.44	3.27	1.24	0.87	
PL2	1.48	4.62	0.67	4.59	0.73	2.05	0.85	0.8	
PL4	1.04	3.1	0.45	3.05	0.47	2.18	1.18	0.9	
PL5	0.94	2.71	0.38	2.55	0.41	2.67	1.31	0.96	
PL7	0.9	2.68	0.38	2.57	0.4	5.12	1.4	0.85	
PL8	0.8	2.53	0.36	2.3	0.35	2.67	1.22	0.9	
PL9	0.87	2.58	0.38	2.55	0.4	3.42	1.33	0.87	
PL10	0.81	2.31	0.33	2.23	0.33	4.87	1.45	0.78	
PL11	0.78	2.41	0.33	2.21	0.33	2.01	1.19	1	
Average	1	2.9	0.4	2.8	0.4	3.1	1.2	0.9	
St. Dev.	0.19	0.63	0.09	0.66	0.11	1.04	0.16	0.06	
PAAS	0.99	2.85	0.4	2.82	43	9.2	1.4	0.65	

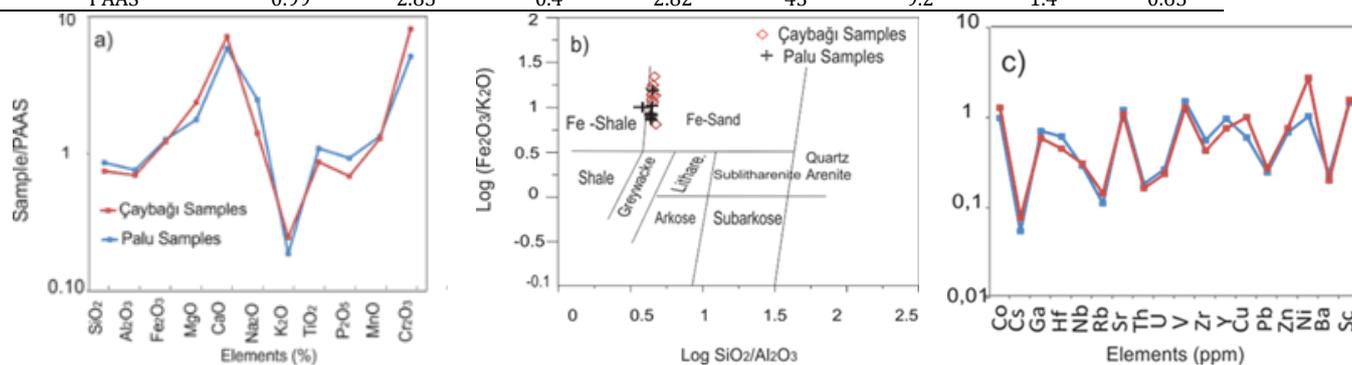


Figure 4: (a): PAAS-normalised distribution of major oxide patterns of samples. PAAS-normalizing values are from [44]; (b): Chemical classification scheme for studied samples (after [43]); (c): PAAS-normalized distribution of trace element patterns of samples. PAAS-normalized values are from [44].

The trace element contents of two sample groups were compared to Post Archean Australian Shale (PAAS; [44]). Th, Zr, and U are initially partitioned to melts through crystallization and for this reason, these elements are enriched in felsic rather than mafic rocks [45]. Sc content is higher at the arc-related mafic rocks [46]. Th, Cs, Zr, Ba, Rb, Hf, Nb, U are lower and Sc, Ni, V and Co concentrations are higher relative to PAAS showing that our samples are do not have an acidic

character (Figure4(c)). Lower Cs, Ba, and Rb contents may reflect also weak weathering and recycling conditions [47].

Correlation analysis can reveal the element associations [48]. Some correlation graphics for major and trace elements are shown in Figure 5. Fe, Na, Ti, and P show positive correlation with Al₂O₃, indicating that these elements are mainly dependent on feldspar and clay minerals (Figure 5(a),(b),(c)). The Zr/Sc ratio is an indicator of heavy mineral concentration [44].

In first-cycle sediments, Th/Sc ratios show a positive correlation with Zr/Sc, on the other hand Zr/Sc ratios in recycled sediments yield variation with slight change accompanying the Th/Sc ratio [49]. There is a significant positive correlation between these ratios in two sample groups, showing that the siliciclastic sample groups are not exposed a considerable amount of sediment recycling (Figure 6).

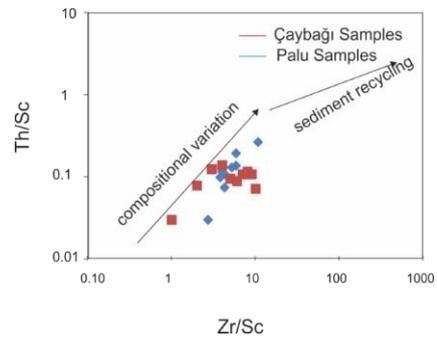


Figure 6: Plot of Zr/Sc vs. Th/Sc [12].

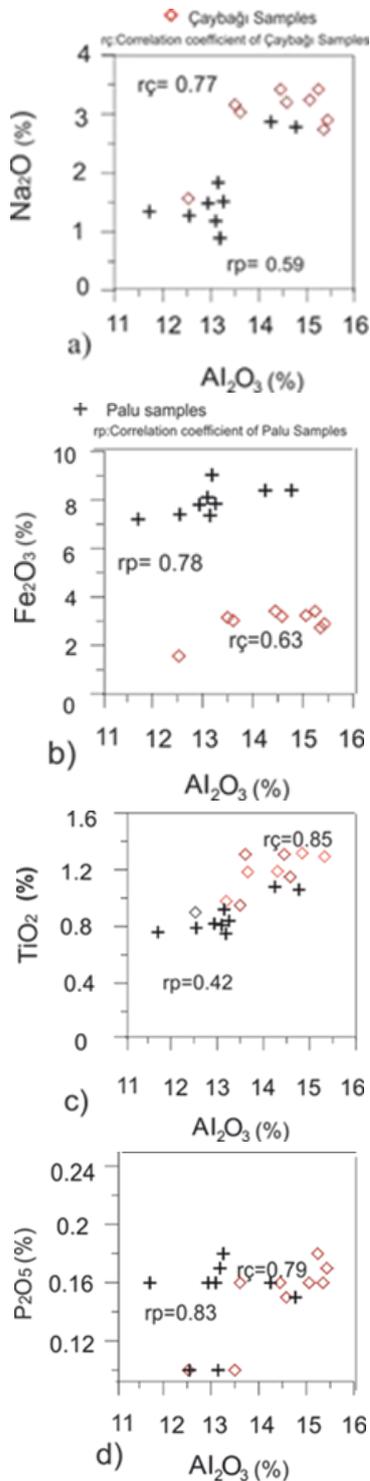


Figure 5: (a); (b); (c); (d): Correlation graphics between some major elements and Al₂O₃.

4.2 REE geochemistry

Concentrations of rare earth elements (REE) are listed in Table 2. Çaybağı and Palu samples have similar REE concentrations. Total REEs show a positive correlation with the group of SiO₂, Al₂O₃, TiO₂, K₂O, P₂O₅, MnO, Cs, Ga, Hf, Nb, Rb, Ta, Th, Y and negative correlation with MgO and CaO in two sample groups. This may indicate that REEs are associated with clay and feldspars (Figure 7a-b). The sorption of REEs by clay minerals was reported by [50],[51]. The negative correlations between total REEs, CaO and MgO are consistent with the decrease in REE concentrations with increasing carbonate content (Figure 7a).

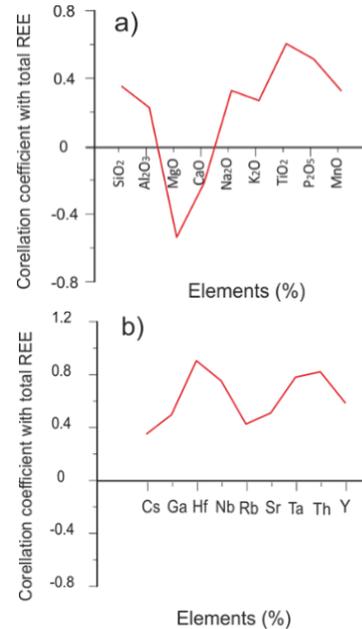


Figure 7: Correlation coefficients between total REEs and (a): Selected major trace elements; (b): Selected trace elements in Çaybağı and Palu samples.

5 Discussion and interpretation

5.1 Provenance and tectonic setting

The geochemical compositions of terrigenous sediments are frequently used by many researchers to infer the provenance, because they tend to reflect source rock composition. Provenance studies are common for sedimentary rocks [7],[8],[53]-[55]. In order to characterize the provenance of shales, it is necessary to rely on elements that are the least mobile during weathering, transport, diagenesis and metamorphism [56].

In geochemical studies, Al/Ti ratios of most clastic sediments display the average composition of the source area [57]. In most igneous rocks, Ti resides in mafic minerals (e.g., pyroxene, hornblende, chlorite, biotite, ilmenite) and Al in feldspars. Al/Ti ratios generally increase with increasing SiO₂ content. Al₂O₃/TiO₂ ratios range from 3 to 11 for mafic rocks, 11-21 for intermediate rocks and 21-70 for felsic rocks [57]. The average Al₂O₃/TiO₂ ratios are 15.33 for Çaybağı and 13.42 for Palu samples showing an intermediate source rock for these samples (Table 1).

In the provenance discrimination diagram of Roser and Korsch [10], the discriminant functions are based on concentrations of immobile and mobile major elements. In this diagram, 4 samples from the Çaybağı Formation plot in sedimentary detrital field and must be taken material from Kırkgeçit Formation (Figure 8). Other samples are in mafic lesser intermediate field. 4 samples from the Palu Formation plot in mafic and lesser intermediate igneous provenance field (Figure 8). As shown from Figure 1b, fluvial deposits of the Hacısamdere member where samples were collected must have been directly fed [42] and received material from Elazığ Magmatics and Kırkgeçit Formation. The materials of the Palu Formation must have been derived from Elazığ Magmatics of intermediate to basic character that is exposed at the east.

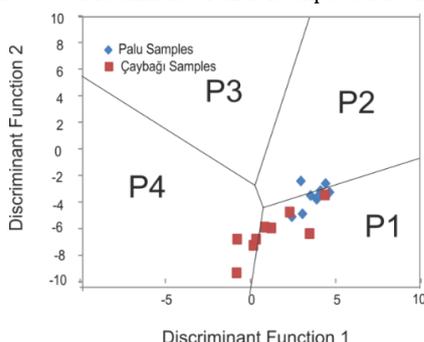


Figure 8: Plot of discriminant functions F1 and F2. [10] divided the boundary values of provenance fields. P1 = mafic and lesser intermediate igneous provenance; P2 = intermediate igneous provenance; P3 = felsic igneous provenance and P4 = recycled-mature polycyclic quartzose sedimentary detritus.

The rare earth elements (REEs) and Ti, Nb, Zr, Y, Sc, Th, and Co are the most suitable for provenance determination of the clastic sedimentary rocks [21],[58],[59]. Geochemical investigations have shown that during the sediment transport and deposition, these immobile elements concentrate in the suspended load of the river, and therefore they are useful for provenance characterization [59],[60]. These elements are transported in terrigenous components of the sediment and they reflect the chemistry of their source rocks [61]. Figure 9(a) compares the TiO₂ vs. Zr of the studied samples, and in the diagram, two groups of samples characterize the intermediate rocks.

La/Sc, Sc/Th, Cr/Th, and Co/Th ratios of immobile elements are also used to determine sediment provenance [44]. La/Sc and Th/Co ratios (Figure 9b) show that two sample groups have similar character (intermediate in composition) lying between acidic and basic rock types. Likewise Sc/Th ratio is also between felsic and basic compositions. Cr/Th and Co/Th are higher than those of basic rocks which can be explained by the enrichment of basic materials during sedimentary processes (Table 3).

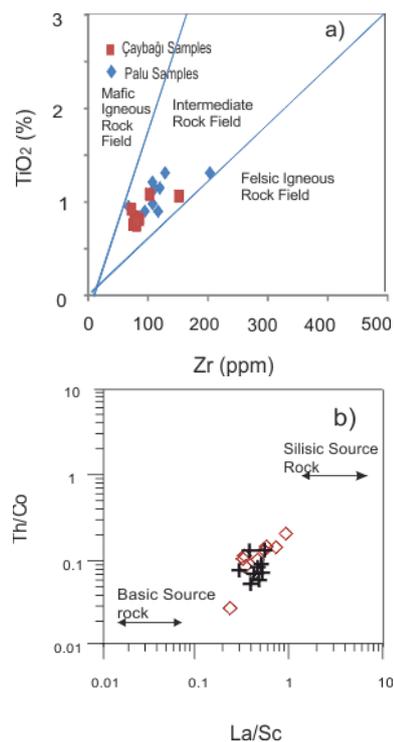


Figure 9: (a): Provenance diagram of TiO₂ vs. Zr in the Çaybağı and Palu samples (after [57]). (b): La/Sc versus Th/Co plot displaying source rock composition for two sample groups (fields after [65]).

Enrichment or depletion of LREEs and HREEs was quantified by the ratio of (La/Yb)_N (N: chondrite normalized; [62]). The average of this ratio is similar for two sample groups, displaying geochemical similarities of Çaybağı and Palu samples (Table 2). Additionally, the REE patterns are also used to estimate the provenance. Basic rocks contain low LREE/HREE ratios and no Eu anomalies, whereas more silicic rocks usually comprise higher LREE/HREE ratios and negative Eu anomalies [63]. Chondrite normalized patterns of sample groups show that REE patterns have low LREE/HREE ratios and little or no Eu anomalies (Figure 10).

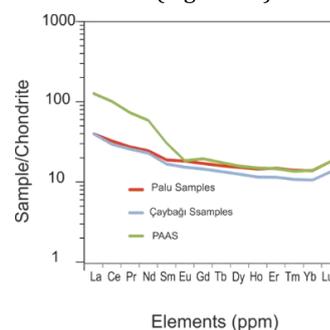


Figure 10: Multielement plot for two sample groups, normalized with chondrite [66].

Eu/Eu* values in two sample groups range from 0.78 to 1, with an average of 0.87, also suggesting an intermediate-mafic source rocks [12],[64]. On the other hand, (La/Yb)_N values are between 4.0 and 3.1 and (Gd/Yb)_N are in the range of 1.4 to 1.2. These values are not compatible with PAAS (Table 2).

These findings also show that the source of two samples groups is intermediate-basic in character. [33] studied the

Elazığ Magmatics around study area, and they suggested that those magmatics are derived from tholeiitic type magmatic rocks which contain basaltic pillow lavas, pyroxene-bearing andesitic lava flows. Sedimentary rocks from different tectonic settings have varying geochemical characteristics [10]. Trace elements and their various bivariate and multivariate plots are mostly suitable for tectonic diagrams of paleotectonic settings [9]. Tectonic environment interpretations for samples based on major element chemistry can be performed using a SiO_2 versus $\text{K}_2\text{O}/\text{Na}_2\text{O}$ diagram [10] (Figure 11a). Samples plot in the fields are grouped as arc related. In the plot of La/Sc vs. Ti/Zr , samples fall in the oceanic island arc field (Figure 11b). As previously stated, Elazığ Magmatics consisting of arc type rocks are the source rock of both groups. Likewise Dönmez [67] suggested that these magmatics were formed in the Late Cretaceous island-arc which is related to the supra-subduction zone of the southern branch of Neotethys.

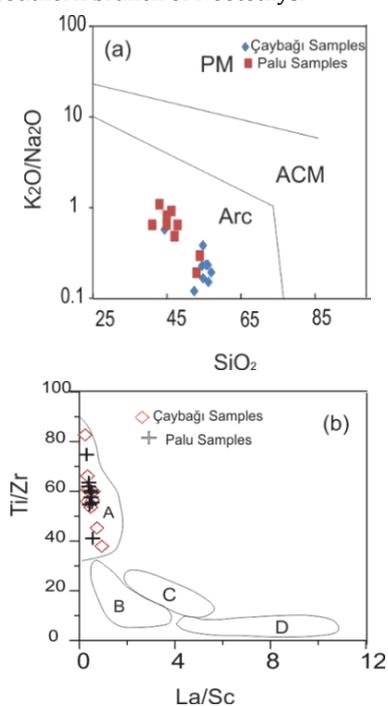


Figure 11(a): Plot of samples on SiO_2 -Log $\text{K}_2\text{O}/\text{Na}_2\text{O}$ diagram of [10]. (b): La/Sc vs. Ti/Zr tectonic discrimination diagram of the samples. Lines represent the fields for sandstones from various tectonic settings (after [9]). A, oceanic island arc; B, continental island arc; C, active continental margin; D, passive margin.

6 Conclusions

Integrated geochemical analyses of samples from the Çaybağı and Palu Formations ensure understanding for the determination of the source rock composition and tectonic setting.

The average $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios are 15.33 for Çaybağı and 13.42 for Palu samples which show intermediate source rocks for these samples.

The provenance discrimination diagram indicates that materials of Çaybağı Formation have been derived from underlying Kırkgeçit Formation of sedimentary character and Elazığ Magmatics. The Palu Formation is greatly contributed from Elazığ Magmatics that consist of intermediate-mafic type rocks.

La/Sc , Th/Co , and Cr/Th ratios display similarity, and comply with sands from basic rocks in two sample groups. Chondrite normalized patterns of two sample groups show that REE patterns have low LREE/HREE ratios, little and no Eu anomalies, and different from PAAS, implying that the source of both sample groups has intermediate-basic in character.

In Si vs. Na/K diagram, samples fall in the arc field. In La/Sc vs. Ti/Zr graphic samples fall in the oceanic island arc field. These findings are in consistent with results of previous investigations on Elazığ Magmatic rocks.

The concentrations of major, trace and rare earth elements (REE) considered are mainly related to the source rock composition and are in accord with provenance rocks of the studied two river systems. Sedimentological investigations suggest that basic-type rocks occur within the drainage basin (e.g. Elazığ Magmatics and Kırkgeçit Formation). consistent with recent interpretation of regional geologic history. The source rocks could be accepted as Kırkgeçit Formation and Çaybağı Formation at the east of Hacısamdere section of Çaybağı Formation, and Elazığ Magmatics at the east of the Palu section. This study presents the initial findings based on a limited number of samples from river deposits from Çaybağı and Palu Formations. Provenance reconstruction could be made by detailed geochemical analyses coupled with mineralogic-petrographic descriptions on vast number of samples collected from different parts of alluvium fan and lacustrine deposits in these basins.

7 Acknowledgement

The financial support of the Fırat University (Turkey) Scientific Research Projects Unit under FUBAP MF.16.13 project number is gratefully acknowledged. We are grateful to the editor and anonymous reviewers whose helpful reviews have greatly improved the manuscript.

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