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Geochemistry of the Zeolite-rich Miocene Pyroclastic Rocks from the Gördes, Demirci and Şaphane Regions, West Anatolia, Turkey

Fahri Esenli[a], Selahattin Kadir[b], *, and Bala Ekinci Şans[a]

[a] *İstanbul Technical University, Department of Geological Engineering, Maslak, İstanbul, TR-34469 Turkey*
[b] *Eskişehir Osmangazi University, Department of Geological Engineering, Eskişehir, TR-26480 Turkey*
**e-mail: skadir.euroclay@gmail.com*

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Abstract—The western Anatolian Miocene volcano-sedimentary basins in the Gördes, Demirci and Şaphane regions host abundant heulandite/clinoptilolite (hul/cpt) bearing widespread zeolitized pyroclastic rocks. Lithostratigraphy of these zeolitic pyroclastic levels show comparable association. Petrography and geochemistry of all the samples show mainly rhyolithic and rhyodacitic character and ash size vitric tuffs. Polarized microscopy and X-ray diffraction determinations of the samples show composition of 55–95 wt % hul/cpt and accessory of smectite, illite/mica, opal–CT, quartz, K–feldspar, plagioclase and opaque minerals. Geochemical results obtained from the studied samples represent hul/cpt–rich facieses formed under the moderate alkaline conditions in these pyroclastic units. Correlation of geochemical results and concentration of hul/cpt in these pyroclastic rocks gives some chemical data on zeolitization process and on adsorption and ion-exchange character of hul/cpt type of zeolites. Depleted and enriched elements by zeolitization have similar ionic radii in general. Ca and H_2O clearly increased, Si, Na and Si/Al ratio decreased in hul/cpt bearing Lower-Middle Miocene pyroclastic rocks of western Anatolia. Additionally, Sr, Nb, Th, Ni, Hf, Cs, Pb and Ta increased, and Zr, Co, W and most of the rare earth elements (REE) decreased in highly hul/cpt–rich pyroclastics.

Keywords: zeolite, clinoptilolite, heulandite, geochemistry, Miocene, Turkey

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INTRODUCTION

The pyroclastic rocks having high content of volcanic glass and porosity are widely transform to zeolite–rich rocks in the nature. Numerous parameters play role for the formation of zeolites in the primary materials; such as fluid parameters (silica activity, cation concentrations, pH, Eh, alkalinity), temperature, pressure, chemistry of parent rock, rock–solution interaction time and types of the hydrological system/geological environment (Iijima, 1978; Surdam and Sheppard, 1978; Barth–Wirshing and Holler, 1989; Hay and Sheppard, 2001; Chipera and Apps, 2001). As an isostructural zeolite mineral, hul/cpt are usually formed from volcanic glass fragments in pyroclastic rocks in closed or open hydrological systems, deep–sea sediments and hydrothermal zones (Gottardi and Galli, 1985; Hay and Sheppard, 2001). Although there has been a general concept that the cpt has higher Si/Al, Na + K/Ca + Mg ratios and thermal stability than hul, the Si and Al in framework and alkali and earth alkali cations in the extra-framework of hul and cpt are highly variable (Boles, 1972). Therefore, Ca–, Na–, K– and Sr–hul and Ca–, Na– and K–cpt are common in the nature (Coombs et al., 1997).

Zeolite content in rock sample effects its adsorption and ion-exchange capacities due to the open framework of zeolites. Especially, hul/cpt–rich tuffs are commercially attractive due to their low costs and widely uses for agricultural, commercial and environmental applications (Ames, 1961; Loizidou and Townsend, 1987; Mumpton, 1988). The selectivity series for cpt–rich tuffs in some studies are given as: Cs > Rb > K > Na > Li for the alkali elements and Ba > Sr > Ca > Mg for the earth-alkali elements (Hector, California; Ames, 1961); Pb > Cd > Cu > Co > Cr > Zn > Ni > Hg (Owyhee County, Idaho and Ash Meadows, Nevada; Zamzow et al., 1990); Pb > Cu > Zn > Cd > Ni (Beli Plast mine, Bulgaria; Shaheen et al., 2012).

During diverge tectonic of the western Anatolia (Turkey) several volcanic materials bearing deposits developed in E-W and NE-SW trending basins (Yılmaz et al., 2000; Helvacı et al., 2006; Helvacı, 2015). Simav, Gediz, Büyük Menderes, and Küçük Menderes basins are developed E–W trending and Bigadiç, Gördes, Demirci, Selendi, and Uşak-Güre basins are NE–SW trending (Helvacı, 2015). The basement rocks in these regions comprise of Paleozoic metamorphics of Menderes massif and Mesozoic ophiolite

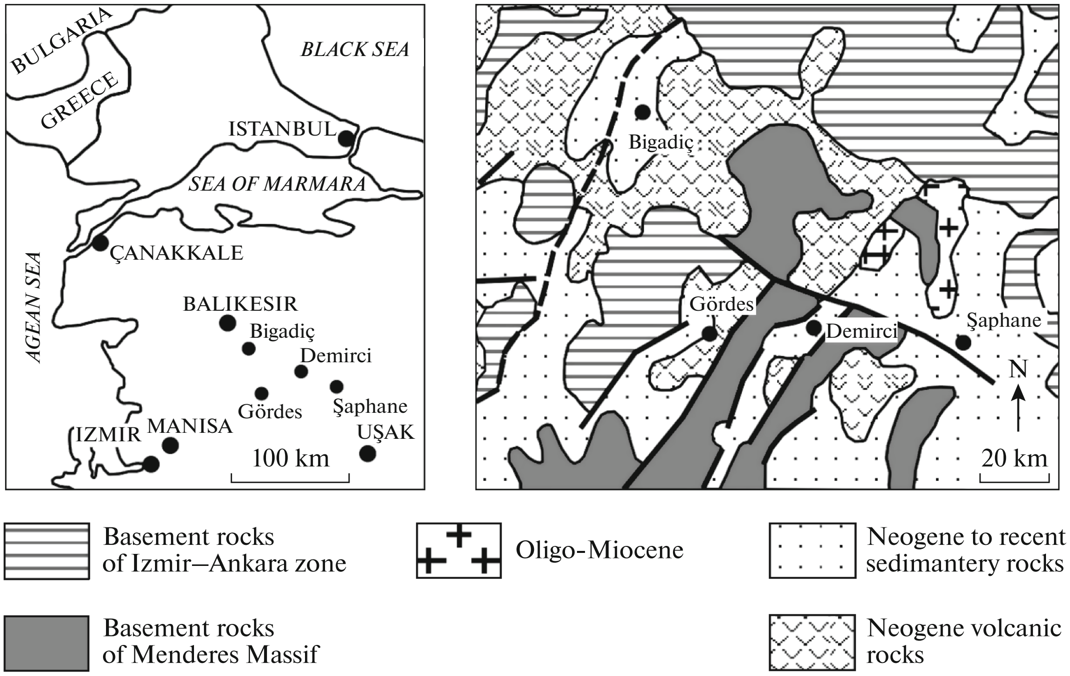

Fig. 1. Location and generalized geological map including studied Miocene basins in west Anatolia (modified from Yılmaz et al., 2000).

and carbonate of the İzmir–Ankara suture zone. Miocene sediment groups are generally originated from massif basement slope, alluvial fan and fluvial materials which continues with the lacustrine sediments. First pyroclastic levels of these basins were formed after deposition of coarse-grained in the lower part of the Miocene units. Most of these levels which were deposited in lacustrine environment have neoform mineral facii including high content of hul/cpt type of zeolites (Esenli, 1993; Snellings et al., 2008; Semiz et al., 2011).

A series of rhyolithic–rhyodacitic tuff including medium and high content of hul/cpt type of zeolite mineral from the pyroclastic levels of three Miocene basins in west Anatolia (Turkey) are the subject of this study (Fig. 1). Representative samples (Gördes: 6; Demirci: 5 and Şaphane: 6) are selected from the dust–ash, glassy tuffs to determine and correlate lithostratigraphic positions, mineralogical and geochemical compositions of pyroclastic rocks based on their concentration of hul/cpt. Although, numerous studies have been reported about major oxides of hul/cpt–rich natural samples, there are no detailed studies on their trace and rare earth elements compositions. Therefore, the aim of this study is to fill this gap and explain the major, trace, and rare earth elements in zeolite-rich tuffs from the west Anatolia in order to determine the chemical changes during the zeolitization processes. This new data on zeolite-rich rocks will provide a critical conclusion about the genetic relationship of hul/cpt group zeolites and their primary volcanic host units. Additionally, this research will guide future exploration and utilization of these zeolite deposits.

ANALYTICAL METHODS

Seventeen samples from the pyroclastic levels of the Miocene sequences in the Gördes, Demirci and Şaphane regions were collected and studied petrographically, mineralogically and geochemically. A polarized-light microscope (Leica) were used for determination of petrographic thin sections of the samples; particularly for definition of texture and primary components. All samples were analyzed by X-ray diffractometer for definition of fine-grained neoform components. X-ray diffraction (XRD) analyses were performed by Bruker D8 Advance instrument with Ni–filtered CuKα radiation at a scanning speed of 1° 2θ/min and a tube voltage of 40 kV and current 40 mA at the laboratory of İstanbul Technical University (Turkey). XRD–reference intensity method (Chung, 1975) was used to determine semi-quantitative modal analyses of the samples by using the reference intensity constants for minerals and steps of methodology given by Ekinci–Şans et al. (2015). The detection limits of mineral concentrations are estimated at approximately 5%.

Chemical analyses of 17 tuff samples were determined by X-ray fluorescence (XRF) method for major elements and inductive couple plasma-mass spectroscopy (ICP–MS) for trace elements at the JAL laboratory of İstanbul Technical University (Turkey). Five grams of sample pulp was crushed to 100–mesh size for these analyses. Pressed discs prepared by binder and boric acid were analyzed using by Bruker S8 Tiger model XRF equipment. Trace element concentrations were determined using Perkin Elmer Elan DRC–e

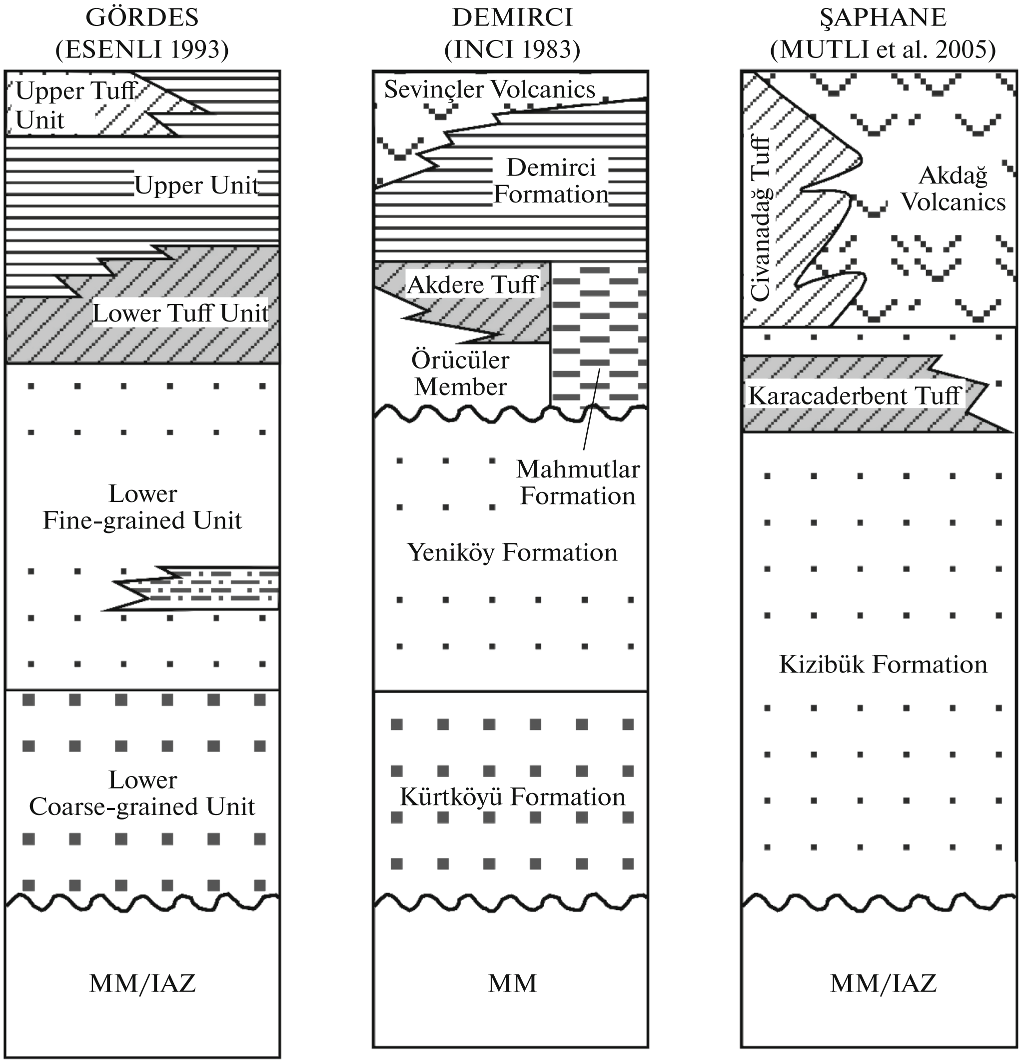

Fig. 2. Comparison of the Miocene stratigraphy of the Gördes, Demirci and Şaphane regions (gray colored ones are zeolite–rich pyroclastic units subjected in this study; MM: Menderes massif, İAZ: İzmir–Ankara suture zone).

6100 ICP-MS instrument. One-tenth gram of sample was treated by acid mixture (3 HCl + 1 HNO_3 + 1 mL HF, 220°C, 40 bar, 1 hour). A 5% boric acid solution was added to the mixture during dissolution. Normalization of REE concentrations was carried out using the North-American Shale Composite (NASC) according to Haskin and Haskin (1966). REE anomalies were calculated from the normalized values of the neighboring REE (for example, the formula of $Ce/Ce^* = 2Ce_N/(La_N + Pr_N)$ given for the Ce anomaly; De Baar et al., 1985).

RESULTS

Geological Setting and Mineralogy

Lithostratigraphic correlation of the Gördes, Demirci and Şaphane regions are shown in Fig. 2. Mineralogical compositions and estimated percentages were determined by XRD semi-quantitative modal analysis method of the samples (Table 1; GR: Gördes, DM: Demirci and SP: Şaphane). Samples are stratigraphically ordered in this table (from bottom to top; 1 to 6 for GR and SP groups and 1 to 5 for DM group). The basement of the study area comprises of Paleozoic Menderes massif and generally limestone and ophiolite complex of Mesozoic İzmir–Ankara suture zone. These units are unconformably overlain by approximately 1000 m Miocene units. Pyroclastic units which is the subject of this study show about 100 m thickness in the regions.

Gördes. Miocene sequence comprises of block–pebble–sand materials at the lower level (lower coarse–grained unit) and continues upward with pebble–sand type sediments in the Gördes region (lower fine–grained unit) and overlain conformably by a volcanic tuff level (lower tuff unit) (Fig. 2; Esenli, 1993). Lacustrine sediments having fine–grain and thin–medium layers of clastic and tuffaceous layers (upper

Table 1. Modal-mineralogical compositions (% in weight by XRD) of the zeolite (hul/cpt)–rich pyroclastic rock samples from west Anatolian (GR: Gördes; DM: Demirci; SP: Şaphane; Hul/Cpt: abbreviation for heulandite/clinoptilolite after Whitney and Evans, 2010). Sample numbers are ordered from bottom to top of the stratigraphy (from 1 to 6 for GR and SP groups and from 1 to 5 for DM group)

Sample	Location	Hul/Cpt	Opal–CT	Quartz	Feldspar	Smectite	Illite/Mica
GR-6	N Gördes; Emede	80–85	10–15	–	–	–	<5
GR-5	N Gördes; Dede hill	75–80	5–10	<5	5–10	<5	–
GR-4	N Gördes; W Kıranköy	80–85	10–15	–	–	<5	–
GR-3	S Gördes; Arkaltı	85–90	5–10	–	–	–	<5
GR-2	N Gördes; Derin stream	80–85	5–10	5–10	–	–	<5
GR-1	S Gördes; Kalabak stream	70–75	10–15	–	–	10–15	<5
DM-5	N Demirci; Soğuksu	85–90	5–10	–	–	<5	<5
DM-4	N Demirci; Akçakayran	85–90	10–15	–	<5	–	–
DM-3	N Demirci; Fatmamezar	85–90	5–10	–	<5	–	<5
DM-2	N Demirci; Gökeşme	85–90	10–15	–	–	–	–
DM-1	N Demirci; Akdere	90–95	–	–	5–10	–	–
SP-6	SW Şaphane; Çırakoğlu	75–80	5–10	<5	<5	–	5–10
SP-5	SW Şaphane; W Köpenez	80–85	5–10	<5	<5	–	<5
SP-4	SW Şaphane; W Köpenez	75–80	5–10	<5	<5	–	5–10
SP-3	SW Şaphane; E Köpenez	55–60	10–15	<5	<5	20–25	<5
SP-2	SW Şaphane; E Köpenez	80–85	<5	<5	<5	5–10	<5
SP-1	SW Şaphane; Köpenez	90–95	<5	<5	–	–	<5

unit) and tuffs which partially mapable (upper tuff unit) overlay the lower tuff unit. Gördes zeolitic (hul/cpt) samples (GR in Tables 1, 2) are from the lower tuff unit. This unit is the main industrial raw material for mining zeolite today and have a continuous several kilometers N–S trending exposures. Thickness (<80 m) and grain size (agglomerate-ash-powder) decrease from north to south. They show rhyolithic-rhyodacitic character, and generally comprise of vitric and ash-dust tuffs. Abundant zeolitic glass shards associated with quartz, plagioclase (albite–oligoclase), K–feldspar, biotite and lithic fragment. K– and Ca–types of clinoptilolites having coarse grain size (10 × 5 × 2 mμ) and high stability (thermally stable up to 700°C) and heulandites having fine grain size and low stability were reported by Esenli (1993) and Esenli and Kumbasar (1998) from the lower tuff unit. XRD determination of GR samples reveal concentration of 70–90% hul/cpt associated with accessory opal–CT, quartz, feldspar, smectite, and illite/mica (Table 1).

Demirci. The lower part of Miocene sequence comprises of block–pebble–sand size of clastics and sandstone–conglomerate, tuffite, mudstone, marl, limestone, and shale in the Demirci region (Fig. 2; Kürtköyü and Yeniköy formations; İnci, 1983). These units continue upward with sandstone, claystone, marl and have lateral transition with pyroclastic rocks (Mahmutlar formation and Akdere tuff). Pyroclastic rocks are covered by sandstone, mudstone, shale (locally bituminous), limestone and tuffite bearing lacustrine unit (Demirci formation) that is laterally and vertically transects with rhyolite-rhyodacite lavas (Sevinçler volcanics). Demirci samples (DM in Tables 1, 2) are related to Akdere tuff. Akdere tuff is widely exposed at the north of Demirci; around Akdere village having approximate 60 m thickness of vitric-crystal and ash-dust tuffs and pumicites. Petrographic determination show that tuff samples composed of mainly glass shards that are completely zeolitized, and associated with K-feldspar, quartz, biotite, muscovite, amphibole, opaque minerals and coarse pumice and lithic fragments. XRD analyses of DM samples show concentration of 85–95% hul/cpt accompanied by opal–CT, feldspar, smectite, and illite/mica (Table 1).

Şaphane. The lower part of Miocene sequence in Simav–Şaphane–Gediz region (Kızılbük formation; Mutlu et al., 2005) consist of sandstone, conglomerate, claystone and tuff levels (Fig. 2). Rhyolithic Civanadağ tuffs and rhyodacitic Akdağ volcanics (Middle Miocene; 14.6 Ma; Seyitoğlu et al., 1997) are located over the Kızılbük formation. Zeolitic tuff level of Kızılbük formation is named as Karacaderbent tuff by Mutlu et al. (2005) and Snellings et al. (2008). Şaphane samples (SP in Tables 1, 2) were obtained from this tuff unit. Tuffs outcrop NE-SW trend between Köpenez and Çavuşoğlukayası hills, SW of Şaphane, having 1 km length and 200 m width. Yellowish green sandstone outcrops at the lowermost of the sequence and exhibit alternation with marl–limestone–claystone at the upper level and have conformable transition with Akdağ volcanics. These volcanics show beige, pale beige, beige-grey, pale green color and generally characterize as vitric rhyolite–rhyodacitic tuffs. Petrographical determination show presence of volcanic ash-dust size glass shard and trace of pum-

Table 2. Major oxides wt %, trace and rare earth elements ppm of the zeolite (hul/cpt)–rich pyroclastic rock samples from west Anatolian (GR: Gördes region; DM: Demirci region; SP: Şaphane region). ΣREE = the sum of (La–Lu) + Y; ΣLREE = the sum of La–Nd; ΣMREE = the sum of (Sm–Ho); ΣHREE = the sum of (Er–Lu); Ce/Ce* = $2Ce_N/(La_N + Pr_N)$, Eu/Eu* = $2Eu_N/(Sm_N + Gd_N)$, Yb/Yb* = $2Yb_N/(Tm_N + Lu_N)$, where N refers to a NASC-normalized value (Haskin and Haskin, 1966)

Sample	GR-1	GR-2	GR-3	GR-4	GR-5	GR-6	DM-1	DM-2	DM-3	DM-4	DM-5	SP-1	SP-2	SP-3	SP-4	SP-5	SP-6
Major oxides, wt %																	
SiO_2	69.50	68.75	66.38	68.20	66.80	64.93	63.87	66.64	66.76	69.44	72.60	64.42	64.02	64.11	64.31	64.98	63.37
Al_2O_3	10.85	11.51	11.64	11.97	11.81	12.07	11.98	11.18	11.11	10.11	11.65	12.34	12.75	12.19	12.56	11.73	12.60
Fe_2O_3	1.08	1.13	0.72	1.24	1.68	1.05	1.64	0.68	0.92	0.43	0.76	1.01	0.97	0.90	1.18	1.14	1.27
MgO	1.09	1.02	0.88	0.87	1.00	0.85	1.01	0.89	0.94	0.62	0.39	1.06	1.16	0.96	1.16	1.08	0.63
CaO	1.95	2.61	3.66	2.08	2.19	2.33	2.43	2.54	2.65	1.82	0.70	2.71	2.70	2.86	2.61	2.27	1.76
Na_2O	0.82	0.26	0.23	0.55	0.88	0.16	0.12	0.11	0.11	0.17	2.92	0.31	0.33	0.18	0.17	0.13	1.15
K_2O	1.72	2.99	2.28	3.91	3.42	4.64	3.80	3.72	3.22	4.68	3.22	3.69	3.43	3.46	3.34	3.66	5.81
TiO_2	0.08	0.07	0.07	0.08	0.08	0.07	0.21	0.08	0.10	0.09	0.07	0.27	0.25	0.24	0.36	0.22	0.23
MnO	–	–	0.01	0.01	0.04	0.01	0.02	–	0.01	0.01	0.01	0.07	0.01	0.01	0.01	0.02	–
P_2O_5	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.02	0.03	0.03	0.03	0.03	0.02	0.03
LOI	13.10	11.70	14.11	11.15	12.28	13.78	14.32	13.94	13.99	12.51	7.65	13.90	14.05	14.35	13.90	14.34	12.79
SiO_2/Al_2O_3	6.41	5.97	5.70	5.70	5.66	5.38	5.33	5.96	6.01	6.87	6.23	5.22	5.02	5.26	5.12	5.54	5.03
$Na_2O + K_2O$/ MgO+ CaO	0.84	0.90	0.55	1.51	1.35	1.51	1.14	1.12	0.93	1.99	5.63	1.06	0.97	0.95	0.93	1.13	2.91
Trace elements, ppm																	
Ni	29.66	33.61	29.88	54.12	40.12	24.72	21.60	27.12	22.39	23.97	26.44	58.44	30.45	34.33	28.12	24.47	31.93
Sc	50.12	48.55	55.34	60.13	59.66	55.57	52.38	55.63	50.42	54.91	46.77	61.12	60.66	59.55	60.11	54.04	54.65
Ba	339	226	351	520	221	140	140	283	366	197	148	1945	1955	1805	2540	825	1200
Be	2.44	2.34	2.88	4.25	1.97	2.59	1.78	2.70	3.32	2.80	2.77	2.80	2.50	3.11	3.24	2.70	2.24
Co	2.99	3.01	3.77	2.56	5.98	2.97	4.26	3.57	3.08	2.96	4.91	3.55	2.20	1.82	3.88	4.21	5.02
Cs	20.66	17.82	17.82	16.71	30.51	29.07	10.18	159.4	156.0	82.67	30.12	11.77	10.77	12.35	9.94	11.69	9.88
Ga	14.75	14.31	14.53	14.41	15.50	13.95	13.77	13.24	15.33	12.42	9.66	13.33	14.26	12.92	13.65	14.28	14.47
Hf	8.11	9.24	8.88	9.55	11.44	11.27	15.71	10.58	10.66	10.31	11.36	15.45	17.77	14.67	13.22	14.74	16.06
Nb	17.63	12.43	14.61	13.57	14.13	14.72	17.26	14.99	19.18	19.24	17.88	18.02	16.62	18.20	17.31	16.91	18.06
Rb	118	135	136	153	178	206	136	340	421	302	330	162	147	165	139	147	165
Sn	8.51	6.33	10.03	8.65	9.12	11.30	6.03	10.96	10.76	7.16	9.78	10.11	12.34	8.10	7.68	8.50	9.71
Sr	427	590	484	330	367	284	880	970	1020	260	241	833	745	907	772	910	422
Ta	1.70	1.18	1.54	1.32	1.20	1.55	1.46	1.76	1.90	1.82	1.68	1.50	1.55	1.58	1.51	1.39	1.43
Th	29.6	29.5	29.2	28.9	32.2	29.5	30.7	26.9	27.8	25.9	28.2	37.5	38.7	37.5	37.8	30.7	30.1
U	45.00	2.62	1.88	4.90	4.20	2.89	7.38	5.36	3.42	6.38	2.60	6.99	5.05	4.15	7.02	7.47	6.17
W	12.5	8.1	6.4	9.5	8.1	19.7	35.4	30.2	16.8	22.6	20.1	9.5	3.7	12.4	12.6	31.9	51.0
Zr	110.2	81.6	72.9	86.2	90.6	90.4	196.0	78.9	86.6	86.9	80.7	187.1	209.1	197.2	186.1	184.1	190.0
Y	85.8	9.2	16.7	10.3	14.6	9.5	19.0	13.4	12.7	18.5	16.6	27.5	25.1	22.9	28.2	17.6	23.3
Ge	0.28	0.12	0.20	0.30	0.10	0.42	0.20	0.22	0.30	0.24	0.26	0.28	0.32	0.57	0.66	–	1.10

Table 2. (Contd.)

Sample	GR-1	GR-2	GR-3	GR-4	GR-5	GR-6	DM-1	DM-2	DM-3	DM-4	DM-5	SP-1	SP-2	SP-3	SP-4	SP-5	SP-6
Mo	0.34	0.28	0.10	0.20	0.44	0.17	0.20	0.48	0.24	0.34	0.44	7.16	11.25	2.00	0.88	0.39	0.45
Cu	4.12	2.33	4.88	2.78	1.58	4.99	2.26	4.64	5.09	2.49	4.88	4.00	4.58	5.87	6.12	6.76	6.66
Pb	36.2	20.7	13.8	38.8	44.4	35.5	42.2	30.8	30.4	34.3	33.6	49.1	48.3	50.2	55.1	56.6	47.5
Zn	30.1	27.3	16.4	26.0	18.8	46.2	44.5	46.0	117.9	97.9	44.1	46.0	90.1	68.7	86.1	98.6	138.4
As	66.1	28.4	30.4	50.5	30.3	80.7	89.0	105.9	85.0	97.0	80.1	42.0	23.5	38.5	64.6	93.6	82.6
Sb	0.45	0.19	0.18	0.20	0.44	0.67	0.68	0.95	0.65	0.59	0.80	0.66	0.75	0.58	0.70	0.74	0.94
Au	0.04	0.02	0.02	0.07	0.02	0.02	0.04	0.10	0.05	0.04	0.05	0.06	0.04	0.03	0.04	0.02	0.02
Ag	0.24	0.26	0.18	0.20	0.27	0.57	0.87	0.50	0.62	0.36	0.48	0.50	0.68	0.87	0.90	1.11	0.95
In	0.03	0.02	0.02	0.03	0.01	0.03	0.01	0.01	0.03	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01
Tl	0.40	0.36	0.39	0.58	0.48	0.68	0.75	0.68	0.31	0.61	0.64	0.60	1.52	0.98	0.55	0.77	0.70
Th/U	0.66	11.28	15.54	5.90	7.69	10.23	4.16	5.03	8.13	4.07	10.85	5.37	7.67	9.04	5.39	4.12	4.88
Rare earth elements																	
La	22.9	21.8	19.2	23.4	20.9	20.3	57.4	22.8	20.9	23.7	26.6	65.8	66.8	66.2	68.6	56.7	59.2
Ce	45.9	43.3	40.1	47.7	46.4	42.1	104.6	43.6	40.7	45.9	55.7	107.5	111.1	107.5	110.0	103.8	101.9
Pr	5.32	4.67	4.43	5.28	4.78	4.87	10.57	4.76	4.57	5.09	5.67	12.30	12.70	12.25	12.65	10.60	10.37
Nd	18.9	16.9	14.9	18.5	17.1	17.7	35.7	16.9	16.3	18.7	18.8	37.5	38.1	37.3	39.6	35.9	36.0
Sm	4.66	3.45	3.79	4.43	3.86	4.11	6.14	3.72	3.58	4.01	3.68	6.12	6.37	5.99	6.37	6.32	6.28
Eu	0.30	0.31	0.20	0.27	0.26	0.14	1.21	0.19	0.24	0.19	0.24	1.13	1.15	1.09	1.10	1.39	1.34
Gd	5.70	3.05	3.34	3.46	3.44	4.36	6.37	3.99	3.60	4.70	4.11	4.72	4.92	4.46	4.80	6.04	6.38
Tb	1.18	0.49	0.60	0.54	0.53	0.47	0.64	0.42	0.42	0.54	0.24	0.72	0.71	0.64	0.75	0.61	0.64
Dy	9.14	2.27	3.08	2.74	3.10	2.84	4.01	2.74	2.73	3.48	2.89	4.58	4.53	4.02	4.72	3.82	4.12
Ho	2.46	0.31	0.53	0.38	0.48	0.35	0.69	0.42	0.43	0.61	0.50	0.95	0.88	0.80	0.94	0.62	0.75
Er	8.50	0.81	1.42	0.97	1.38	1.08	2.41	1.64	1.54	2.19	1.71	2.77	2.45	2.24	2.86	2.09	2.72
Tm	0.15	0.10	0.21	0.14	0.22	0.02	0.23	0.14	0.11	0.20	0.18	0.45	0.39	0.34	0.44	0.18	0.30
Yb	10.50	0.66	1.26	0.89	1.69	0.90	2.17	1.72	1.57	2.09	1.70	3.06	2.50	2.21	2.85	1.91	2.78
Lu	1.73	0.10	0.21	0.13	0.24	0.03	0.21	0.14	0.12	0.18	0.15	0.48	0.37	0.33	0.44	0.15	0.31
REE	223.2	107.6	110.1	119.2	119.2	109.1	251.5	116.8	109.6	130.2	139.1	275.6	278.1	268.4	284.4	247.9	256.6
LREE	93.1	86.8	78.7	95.0	89.3	85.2	208.4	88.2	82.5	93.5	107.0	223.2	228.7	223.3	230.9	207.1	207.6
HREE	20.88	1.67	3.10	2.13	3.53	2.03	5.02	3.64	3.34	4.66	3.74	6.76	5.71	5.12	6.59	4.33	6.11
MREE	23.44	9.88	11.54	11.82	11.67	12.27	19.06	11.48	11.00	13.53	11.66	18.22	18.56	17.00	18.68	18.80	19.51
LREE/HREE	4.46	51.97	25.39	44.58	25.31	41.95	41.50	24.24	24.71	20.07	28.61	33.01	40.06	43.61	35.04	47.83	33.98
Eu/Eu*	0.25	0.42	0.25	0.30	0.31	0.14	0.85	0.22	0.29	0.19	0.27	0.92	0.90	0.92	0.87	0.99	0.93
Ce/Ce*	0.90	0.93	0.95	0.93	1.01	0.92	0.92	0.91	0.91	0.91	0.98	0.82	0.82	0.81	0.80	0.91	0.88
Yb/Yb*	1.74	1.04	0.95	1.04	1.16	5.66	1.56	1.94	2.16	1.74	1.63	1.04	1.04	1.04	1.02	1.83	1.44
LaN/YbN	0.21	3.20	1.48	2.55	1.20	2.19	2.56	1.29	1.29	1.10	1.52	2.08	2.59	2.90	2.33	2.88	2.06

ice and mineral fragments. Mineral fragments such as plagioclase, K-feldspar, quartz, and biotite generally show concentration of <10%. XRD analyses of SP samples show concentration of 55–95% hul/cpt accompanied by minor to trace opal–CT, quartz, feldspar, smectite, and illite/mica (Table 1). Smectite enhance up to 25% in only one level.

Geochemistry

Chemical analyses of hul/cpt–rich tuff samples from the Miocene Gördes, Demirci and Şaphane basins (GR, DM and SP groups) are given in Table 2. The samples from all regions have range of SiO_2 (63.37–72.60), Al_2O_3 (10.11–12.75), Fe_2O_3 (0.43–1.71), MgO (0.39–1.16), CaO (0.70–3.66), Na_2O (0.07–3.63), K_2O (1.48–5.81), TiO_2 (0.05–0.36), and LOI (7.65–14.93 wt %). Totals of MgO+CaO and Na_2O+K_2O vary from 1.09 to 4.11 wt % and 1.55 to 6.96 wt % and the ratios of SiO_2/Al_2O_3 and Na_2O + K_2O/MgO + CaO vary from 5.02 to 6.41 and, 0.42 to 5.63, respectively. The samples show calc-alkaline (mainly high–K calc–alkaline) character according to K_2O + Na_2O–FeO–MgO (AFM) diagram (Fig. 3a; Irvine and Baragar, 1971) and K_2O–SiO_2 diagram (Fig. 3b; Peccerillo and Taylor, 1976). The samples appear in rhyolite–rhyodacite/dacite–trachyandesite–trachyte boundaries on the Nb/Y–Zr/TiO_2 diagram of Winchester and Floyd (1977) (Fig. 3c). Compositions close to the trachyte and trachyandesite in this diagram are controversial because of the Y mobilization; decreasing during zeolitization in general (Christidis, 1988). Thus, the samples may be considered as rhyolite–rhyodacite that is supported by the petrographical determination.

Demirci (DM) samples have higher alkaline characters among the three regions [Na_2O + K_2O/MgO + CaO: 0.93–5.63 (average 2.16) in DM; 0.84–1.51 (average 1.11) in GR and 0.93–2.91 (average 1.33) in SP samples; Table 2]. They have also higher ratios of SiO_2/Al_2O_3 and lower Ca and Mg than GR and SP samples. This is probably related to the different chemical compositions of circulating solutions through the host rocks between the regions. In this manner, Demirci Miocene basin is underlain by Si–, Na– and K–rich metamorphics of the Menderes massif (MM) basement rocks (Fig. 2). Ca– and Mg–rich basement group; the Mesozoic İzmir–Ankara suture zone (IAZ) including limestone and ophiolite complex is absent in Demirci basin, while it is present in Gördes and Şaphane basins (Fig. 2). On the other hand, in the studied samples, Ba and Sr have elevated in Ca–rich samples probably due to Ba and Sr substituted for Ca easier than Na in the zeolite structure. Major oxides, Ba, Sr, Rb, Zr and Ni of all studied samples generally show low-medium negative correlation with SiO_2 (Fig. 4). There is clear negative correlation between SiO_2 with each of Al_2O_3, Fe_2O_3, MgO, CaO, and K_2O. The SP samples show different accumulation on some diagrams and composed of low SiO_2 and high Al_2O_3, MgO, K_2O, TiO_2, Ba, Sr, and Zr. GR and DM samples show wide but SP samples narrow distribution on Harker diagrams.

Trace and REE contents of the hul/cpt–rich pyroclastic rock samples were normalized to the N-MORB (Sun and McDonough, 1989; Fig. 5a) and chondrite values (Boynton, 1984; Fig. 5b). Trace element profile of the samples illustrates homogeneity and enrichment for light REE (LREE) and inhomogeneity for medium REE (MREE) and partly flat for heavy REE (HREE). The samples exhibit negative anomalies of high-field strength elements (HFSE), especially in Nb, P and Ti relative to adjacent LILE and LREE and UCC. Th, K and Pb exhibit positive anomalies. MREE and HREE generally show flat pattern. Samples of the Gördes, Demirci and Şaphane regions have negative Eu anomaly (Eu/Eu* = 0.14–0.99) relative to chondrite. Most of the trace elements were enriched in Şaphane pyroclastic rocks (SP samples) compared to the other regions. The ΣREE, LREE, MREE and HREE are higher in SP than GR and DM samples and also Eu/Eu* is clearly higher (0.87–0.99) than those of GR (0.14–0.42) and DM (0.19–0.85). Th/U ratios of the samples (Table 2; 4.07–15.54, except one sample; 0.66) revealed altered source according to the average Th/U ratio of UCC (3.8; Taylor and McLennan, 1985; Condie, 1993; McLennan, 2001).

Some REE findings; particularly negative Nb, P and Ti and positive Th, K and Pb anomalies address contamination of crustal material and island arc volcanics and subduction-related origin (Weaver and Tarney, 1984; Hofmann, 1988). The samples plot completely on the active continental margin (ACM) field in the Th/Ta–Ta/Yb and Th/Hf–Ta/Hf geotectonic diagrams given of Schandl and Gorton (2002) (Fig. 6). Additionally, the samples plot as a line into the volcanic arc array on the Th/Yb–Th/Yb variation diagram of Pearce (2008) (Fig. 7). These results exhibit similarity to the Miocene calc-alkaline volcanics from the west Anatolia reported by Seyitoğlu and Scott (1992), Mutlu et al. (2005), Ersoy et al. (2008, 2014) and Kaçmaz (2016).

DISCUSSION

Zeolite (hul/cpt)–rich pyroclastic rocks from the Miocene Gördes, Demirci and Şaphane basins are probably stratigraphic equivalent of each other. Purvis et al. (2005) reported 19.16 ± 0.09–17.04 ± 0.35 Ma based on Ar/Ar radiogenic aging of biotites and sanidines from pyroclastic rocks of Gördes (lower tuff unit of this study; lacustrine tuff facii of Purvis and Robertson, 2004; Güneşli volcanics of Ersoy et al., 2011). The ages of 19.75 ± 0.07–19.06 ± 0.05 Ma (Ar/Ar) for dacitic Sevinçler volcanics and 17.58 ± 0.09 Ma (Ar/Ar) for andesitic Asitepe volcanics from the

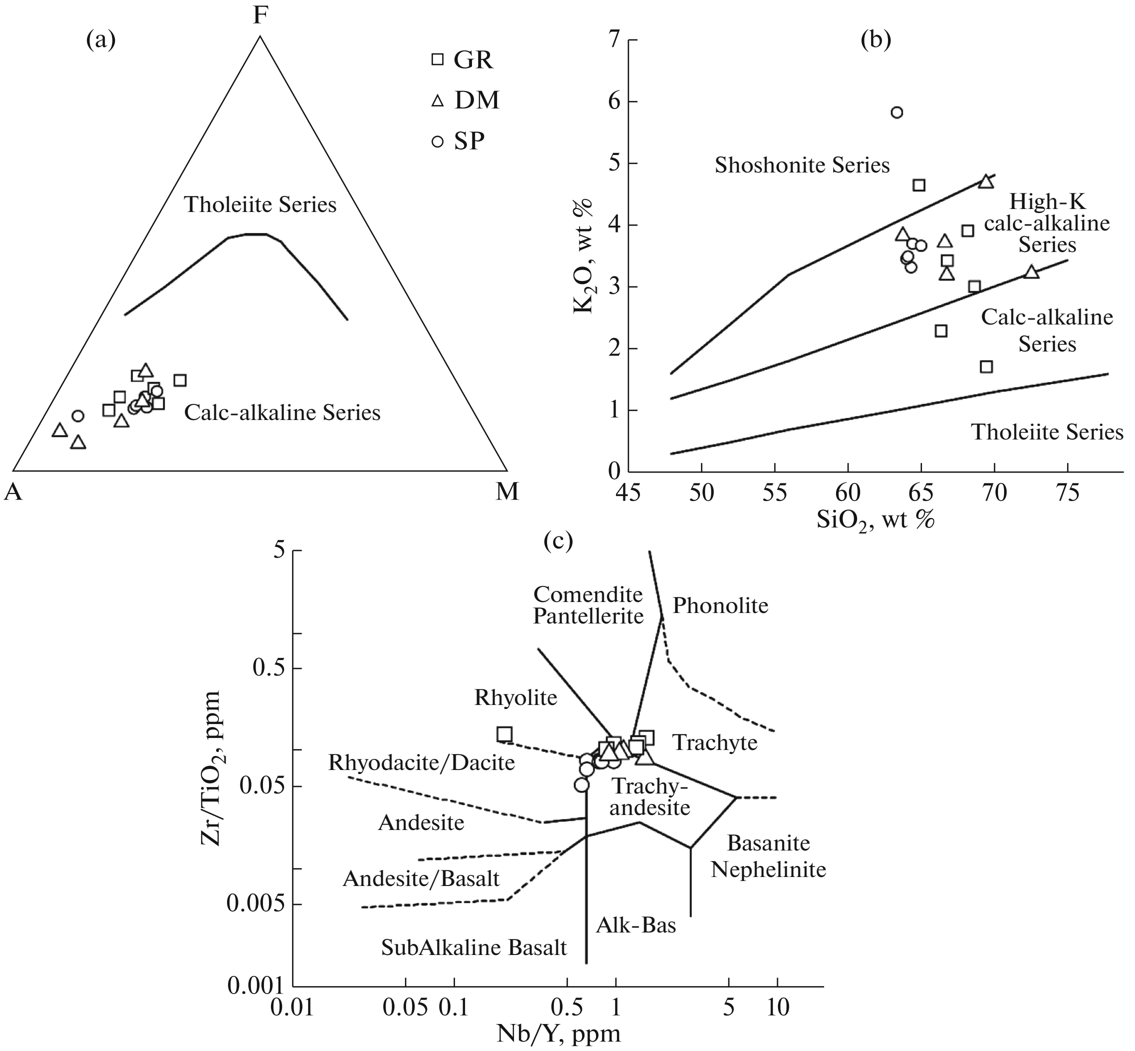

Fig. 3. Discrimination and classification diagrams for the zeolite (hul/cpt)–rich pyroclastic rocks from the Miocene Gördes, Demirci and Şaphane basins in west Anatolia: (a) K_2O+Na_2O–FeO–MgO (AFM) diagram (Irvine and Baragar, 1971), (b) K_2O–SiO_2 diagram (Peccerillo and Taylor, 1976), (c) Nb/Y–Zr/TiO_2 diagram (Winchester and Floyd, 1977).

Demirci basin were given by Ersoy et al. (2012). Stratigraphically, zeolitic Akdere tuff in Demirci basin is located between these two volcanic units. Additionally, rhyolite of Akdağ volcanics in the Gediz-Şaphane region was aged as 20.30 ± 060–19.00 ± 0.2 Ma (K/Ar aging; Seyitoğlu et al., 1997; Helvacı and Alonso, 2000). Ersoy et al. (2011, 2014) reported 20.00 ± 0.20–17.90 ± 0.20 Ma (K/Ar and Ar/Ar) from the dacitic-rhyolithic Eğreltidağ volcanics at the bottom of andesitic-dacitic Yağcıdağ volcanics of Selendi Miocene basin, close to Demirci and Şaphane regions. The authors also explained these volcanics were equivalent to the Güneşli volcanics of Gördes and Sevinçler volcanics of Demirci and also Akdağ volcanics of Emet basins.

Generally, fluid composition and temperature are important factors on development of zeolite paragenesis. Also, alteration of volcanic rocks containing natural glass as a reactive phase generally associated with low-temperature (<300°C), neutral to alkaline waters, and most of the zeolite minerals were found only at temperature below 200°C (Chipera and Apps, 2001). Zeolitization processes in the studied basins possibly developed in the same or close periods, similar geologic-hydrologic lacustrine environments and also under the similar physico-chemical conditions at low-temperature. The lakes in the studied regions at the Miocene epoch can be defined as rift system alkaline lakes in the concept of closed hydrologic system (Surdam, 1977; Langella et al., 2001). Therefore, the waters feeding these lakes are derived from underground springs. Zeolite mineral paragenesis show similarity in the Gördes, Demirci and Şaphane regions. However, it is reported that the lower and upper levels of the zeolite-rich tuffs from Gördes and Şaphane basins partly contain different neoform minerals (opal–CT, quartz, smectite, K–feldspar) and hul/cpt with different exchangeable cations (Esenli, 1993;

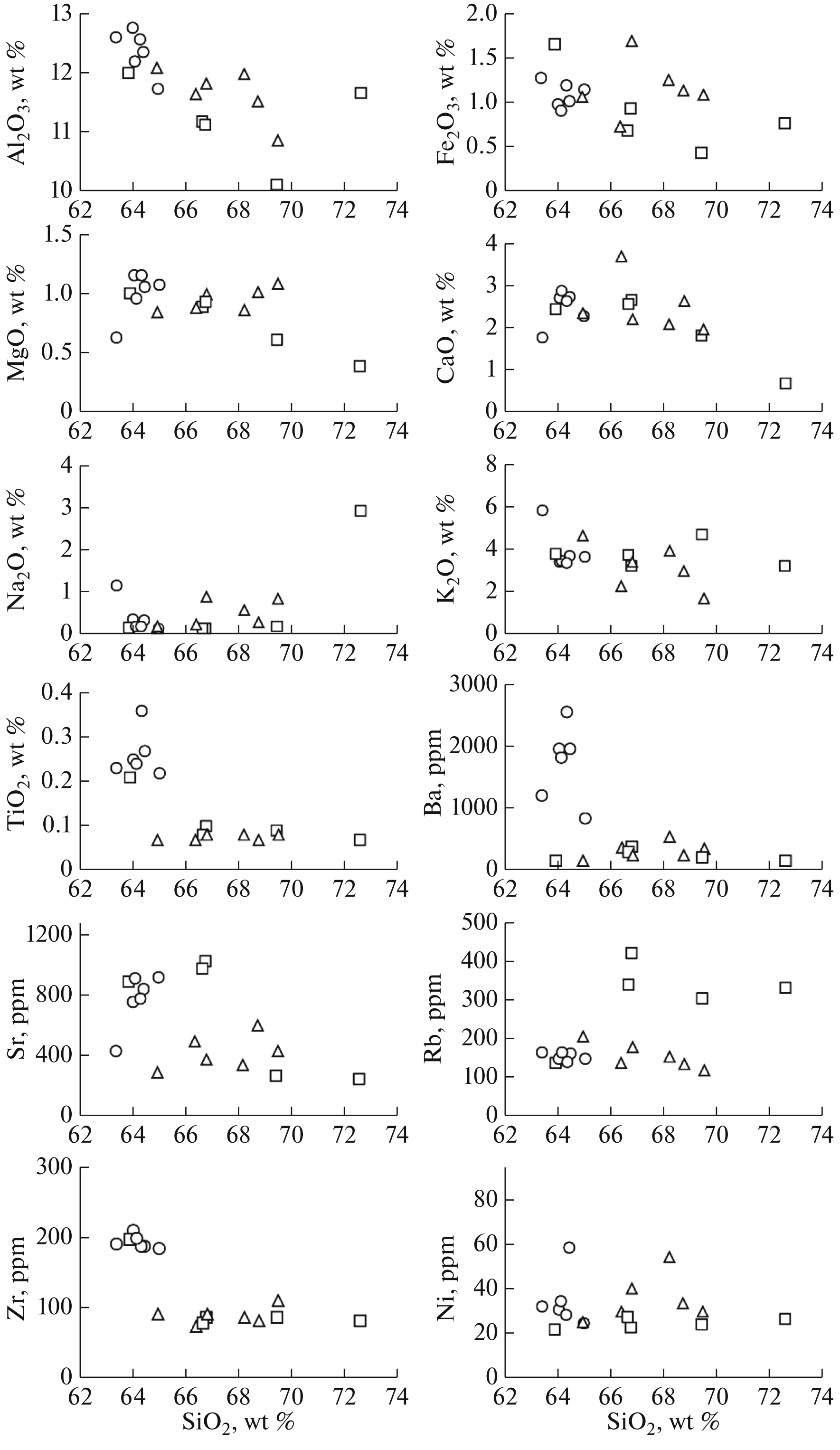

Fig. 4. Harker diagrams for major oxides and some trace elements versus SiO_2 for the pyroclastic rocks from the Miocene Gördes, Demirci and Şaphane basins in west Anatolia.

Snellings et al., 2008). Major oxides of the zeolite-rich tuff samples address Si–rich and K– and/or Ca–rich types of hul/cpt in the Gördes, Demirci and Şaphane regions. Although, SiO_2/Al_2O_3 ratios show homogeneity, ratios of alkaline/alkaline-earth cations show heterogeneity. Na–rich hul/cpt levels are rarely found in the studied pyroclastic rocks. Increasing and decreasing of some elements are related to: (1) chemistry of the vol-

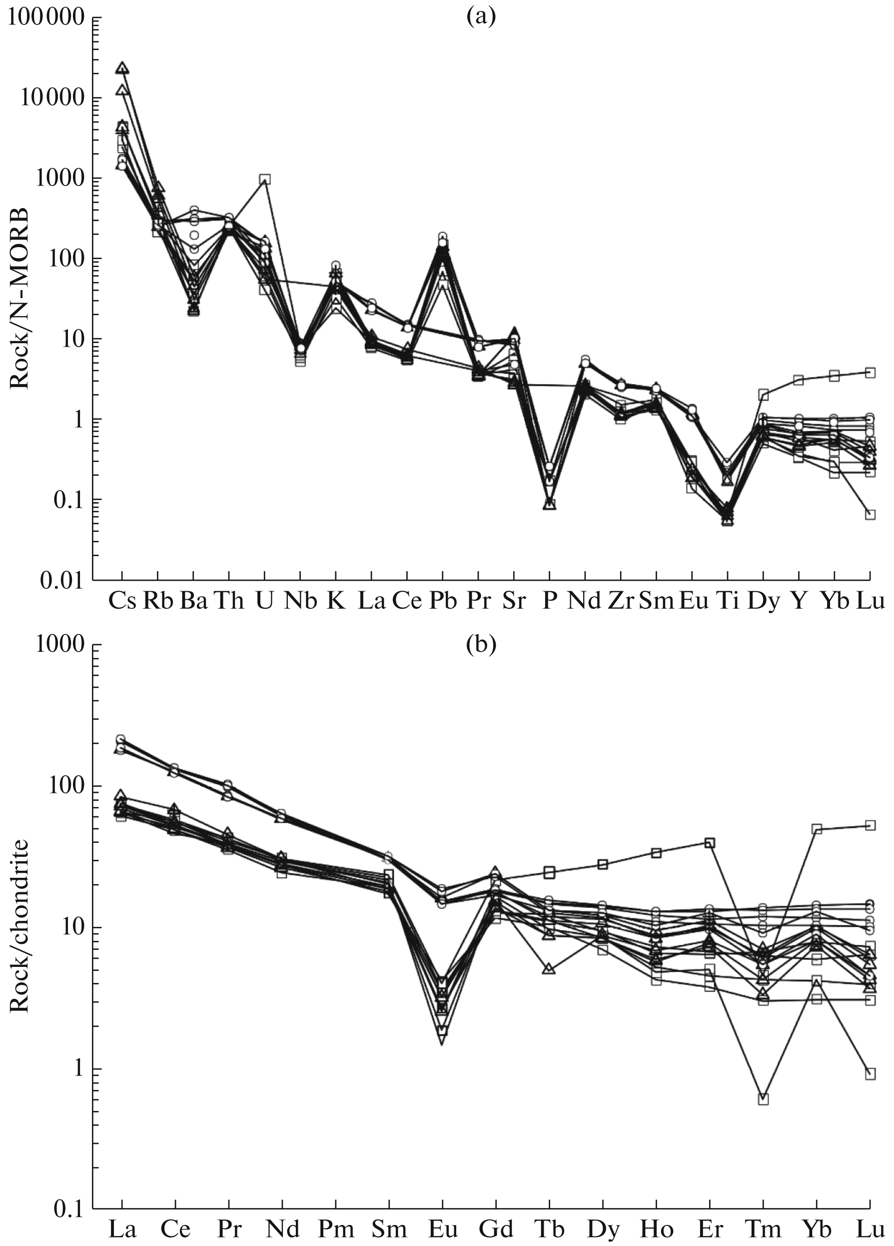

Fig. 5. (a) N–MORB normalized trace element (Sun and McDonough, 1989); (b) chondrite–normalized (Boynton, 1984) REE spider diagrams for the pyroclastic rocks from the three Miocene basins in west Anatolia.

canic primary materials, (2) the stability constants of these elements in the solution after deposition of the pyroclastic rocks, and (3) the properties of atomic substituents in hul/cpt extra–framework structure.

Essentially, trace element chemistry of pyroclastic rocks from the Gördes, Demirci and Şaphane regions show some differences. For example, Ba, Hf, Sr, Zr, Mo, Cu, Pb, Zn, Ag, ΣREE, ΣLREE, ΣHREE, ΣMREE, ratio of ΣLREE/ΣHREE and Eu/Eu* are higher in the Şaphane (SP) samples (Table 2). Cs, Rb, Yb/Yb* values in Demirci (DM) samples are higher than those of the other regions. As a local or stratigraphic difference, chemical values of sample GR-1 from the lowermost of the lower tuff unit in the south of Gördes is different from the other Gördes (GR) samples (Fig. 2; Table 2). U, Y and ΣHREE values of this sample is about ten time more than the others, in contrast, Th/U and LaN/YbN values are about ten time less. It is known that the sandstones of the lower fine- and coarse-grained units (Fig. 2) are rich in U in the equivalent stratigraphic levels in the nearby region (south of Gördes; Köprübaşı uranium deposits; Yılmaz, 1982). U anomaly of this sample is probably related to this regional feature.

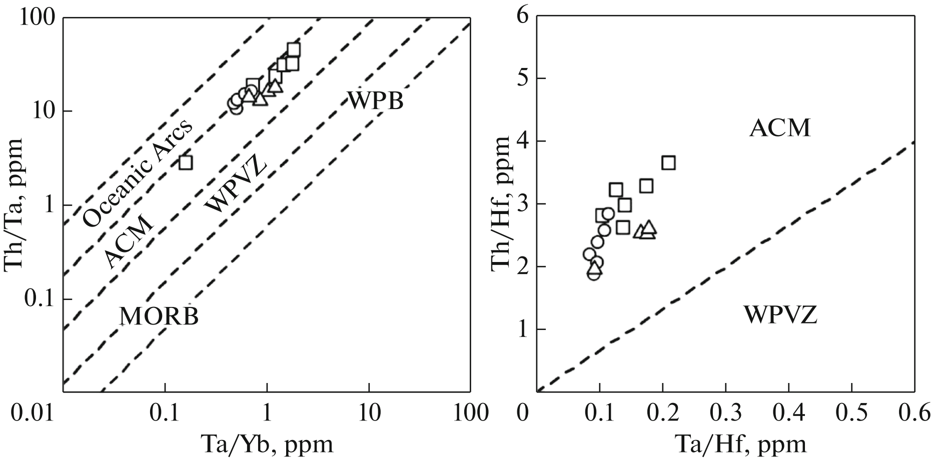

Fig. 6. Plots of the pyroclastic rocks samples from the Miocene Gördes, Demirci and Şaphane basins in west Anatolia on the Th/Ta–Ta/Yb and Th/Hf–Ta/Hf geotectonic diagrams given by Schandl and Gorton (2002) (ACM: active continental margin, WPVZ: within–plate volcanic zone, WPB: within-plate basalt, MORB: mid–ocean ridge basalt).

Chemical compositions and types of the zeolite-group mineral in between fresh and zeolitic rocks also depend on the character of their parent rocks. For example, chemical changes show difference between zeolite–rich andesitic–latitic parent rocks from zeolite–rich rhyolithic–dacitic ones (Walton, 1975; Barrows, 1980; Tsolis-Katagas and Katagas, 1989; Tsirambides et al., 1993; Esenli, 1993; Snellings et al., 2008). Some chemical changes during the zeolitization of tuffs are summarized in Table 3. All zeolitic tuff units are rhyolithic–rhyodacitic in character in Table 3. According to Iijima (1971), Walton (1975) and Tsirambides et al. (1993), although, some major oxides have different character, SiO_2 and K_2O significantly depleted from fresh host rocks to clinoptilolitic-bearing altered rocks of Japan, USA and Greece, respectively (Table 3). Esenli (1993) and Snellings et al. (2008) emphasized that CaO, MgO and H_2O increased, while SiO_2, Na_2O and K_2O decreased during zeolitization process of cpt-bearing tuffs in Gördes and Şaphane regions (Turkey), respectively (Table 3). Moreover, Esenli (1993) underlined that these changes are higher in hul–rich tuffs compared to cpt-rich ones and Ba, Sr, La, B, U, Th, As, P and Zn values are approximately double in hul/cpt–rich facii, while Mn, Co and W values increase in non–zeolite facii and Ba, Sr, La, and B values are relatively higher in hul–rich samples compared to the cpt–rich ones. Erdem–Şenatalar et al. (1992) concluded that K_2O, CaO and MgO increased and SiO_2 and Na_2O decreased with increasing of zeolite content from Bigadiç zeolitic tuffs. Also, Gündoğdu et al. (1996) reported zeolitic (K– and Ca–cpt) and non-zeolitic (mainly glass + smectite) samples from Bigadiç and Emet basins (Turkey). Their zeolitic samples have higher SiO_2, Al_2O_3, CaO and MgO values and lower Na_2O, K_2O and Fe_2O_3 values compared to that of non-zeolitic ones (Table 3). Recently, Kaçmaz (2016) explained a correlation between zeolitic and non-zeolitic tuffs from Demirci region (Yenice–Saraycık area). According to the author, rhyodacitic–rhyolithic tuffs with high amounts of hul/cpt contain higher Mg, Ca, P and LOI but lower K, Na and Mn than those of unaltered tuffs. The author also revealed that there is no big change in the REE abundances of unaltered and hul/cpt–rich tuffs although Ba, Sr, Cs, Pb, Zn, Ni, As, and Sb are higher in zeolitic tuffs and U in unaltered tuffs.

The studied zeolitic tuff samples from Gördes, Demirci and Şaphane show concentration range of 55–95 wt % hul/cpt (Table 1). Therefore, it is difficult to clear correlate zeolitic units with the pyroclastic

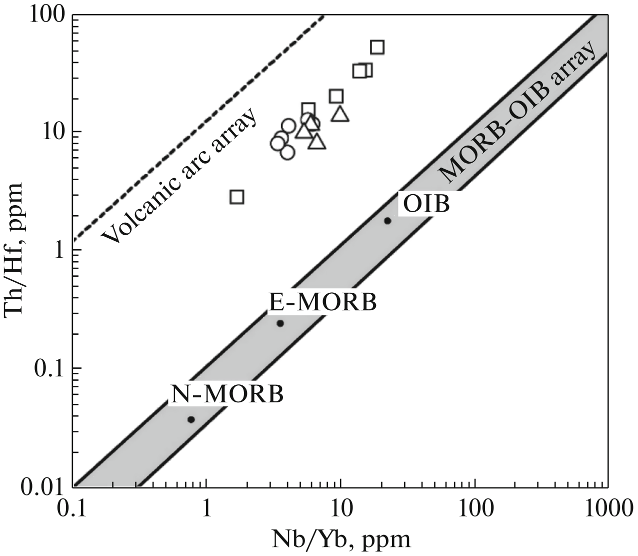

Fig. 7. Plots of the pyroclastic rocks samples from the Miocene Gördes, Demirci and Şaphane basins in west Anatolia on the Th/Yb *vs* Th/Yb variation diagram of Pearce (2008).

Table 3. Major oxides changes during zeolitization in some hul/cpt–rich rhyolithic–rhyodacitic tuffs in the world

Reference	Region	Component gained	Component depleted
Iijima (1971)	Hokkaido (Japan)	Al_2O_3, Fe_2O_3, MnO, MgO, H_2O	SiO_2, CaO, Na_2O, K_2O
Walton (1975)	Trans-Pecos (USA)	CaO, Na_2O	SiO_2, K_2O
Tsirambides et al. (1993)	Metaxades (Greece)	Fe_2O_3, CaO, MgO, Na_2O	SiO_2, K_2O
Erdem-Şenatalar et al. (1992)	Bigadiç (Turkey)	CaO, MgO, K_2O	SiO_2, Na_2O
Esenli (1993)	Gördes (Turkey)	CaO, MgO, H_2O	SiO_2, Na_2O, K_2O
Gündoğdu et al. (1996)	Bigadiç, Emet (Turkey)	SiO_2, Al_2O_3, CaO, MgO	Fe_2O_3, Na_2O, K_2O
Snellings et al. (2008)	Şaphane (Turkey)	CaO, MgO, H_2O	SiO_2, Na_2O, K_2O
Kaçmaz (2016)	Demirci (Turkey)	CaO, MgO, H_2O	Na_2O, K_2O, MnO
This study (all samples)	Gördes, Demirci, Şaphane (Turkey)	CaO, H_2O	SiO_2, Na_2O

parent rock. However, comparison of 55–75 wt % hul/cpt bearing samples (GR–1 and SP–3) and 75–95 wt % hul/cpt bearing other samples show that CaO and LOI increased, while SiO_2 and Na_2O decreased with increase concentration of hul/cpt. In Gördes samples Al_2O_3, CaO, K_2O and LOI values are higher and SiO_2, Fe_2O_3, MgO, and Na_2O values are lower relative to enhance of hul/cpt. In Demirci samples SiO_2 and Na_2O values decrease, in contrast Al_2O_3, Fe_2O_3, MgO, and CaO values increase during zeolitization. It is difficult to determine Şaphane samples; partly MgO increasing with increasing of hul/cpt concentration is seen in these samples. It can be summarized that the total of alkaline–earth elements (particularly Ca^{2+}) increased and alkaline elements (particularly Na^+) decreased in pyroclastic rocks of the studied basins. These types of gains and losses reveal that hul/cpt type of zeolitization in the studied basins suggest development under the moderate alkaline conditions near the center of the basin (pH: 7–9; Mariner and Surdam, 1970; Hay and Sheppard, 2001). For example, high alkaline zeolites (analcime) and K-feldspar were reported from the center of the Gördes Miocene basin by Esenli (1993). Therefore, hydrolysis of volcanic glass in the pyroclastic rocks of Gördes, Demirci and Şaphane basins are controlled by the solution chemistry, rise of pH due to the reaction between the alkaline cations and water. Thus, devitrification of volcanic glass resulted firstly formation of gel-like phase and that is later of converted to hul/cpt types of zeolites.

In addition to the major oxide changes during zeolitization of the studied pyroclastic rocks, REE compositions show variable values. Although, LREE shows similarity, totally and individually all MREE and HREE increased in higher zeolitic sample SP-1 (90–95% hul/cpt) and SP-3 (55–60% hul/cpt) samples in Şaphane (SP) (Tables 1 and 2; Fig. 5). The mobility of MREE and HREE relative to LREE is also seen in the GR samples. DM samples show mobility for all REE. On the other hand, Ersoy et al. (2008) reported the chemical composition of non-zeolitic Eğreltidağ volcanics which is overlain by Akdere tuff in Demirci basin show different chemistry from Demirci and Gördes zeolitic tuffs. If we accept that Eğreltidağ volcanics is related with Demirci-Akdere tuff and also Gördes-lower tuff unit, thus, Sr, Nb, Th, Ni, Hf, Cs, Pb, and Ta increased and Zr, Co, and W and most of the REE and also some major elements (Al, Fe, Ca, Na) decreased by increase of hul/cpt via zeolitization process.

The sorption of some elements in hul/cpt–rich pyroclastic rocks should be controlled mainly by ion-exchange reactions. During or following zeolitization process some elements having similar ionic radii (e.g. Na–Ca, Ca–Sr, K–Ba and Mg–Fe) probably more easily substituted each other. Some trace elements showing depletion or enrichment have also similar ionic radii. Some other substitutions such as Mg–Cu–Ni–Zn–Co–Fe–Cr, Ca–HREE+Y, W–Ti–Zr–Hf and Pb–Th–U are probably controlled and resulted to depletion–enrichment in zeolitic rocks. Particularly, most of the radionuclides are higher in hul/cpt–rich facii of pyroclastic rocks because of the greater selectivity of zeolites for these elements. Simmons and Neymark (2012) also reported that sorption of Sr, Cs, Th, and U is also found in more pronounced in cpt-rich tuffs than vitric tuffs of Yucca Mountain (USA). REEs having smaller ionic radius i.e. heavier lanthanides easily exchanged by changeable major cations of hul/cpt and Y may be more effective among them. Thus, enhance of some major, trace and rare earth elements in west Anatolian hul/cpt–rich tuffs is a function of selectivity of zeolite minerals additionally to the parameters of geological environment.

CONCLUSIONS

Field observation show that the lower tuff unit in Gördes, Akdere tuff in Demirci and Karacaderbent tuff in Şaphane show equivalent lithostratigraphic to each other. All of zeolitic pyroclastic rocks in the regions show similar petrographic characteristics; textures, glass shard (+pumice)/crystal ratio and significantly zeolite mineral types and zeolitization process. Based on both of mineralogy and major oxide chemistry from the studied pyroclastic rocks and related references, chemical gains and losses during the zeolitization (hul/cpt type) of rhyolithic/rhyodacitic tuffs are summarized as: (1) SiO_2 decreases, in contrast Al_2O_3 increases and generally Si/Al ratio decreases. (2) Fe_2O_3 does not show clear change, but MgO generally increases. (3) CaO generally increases and enhance in hul-type alteration. (4) Na_2O decreases and K_2O shows slight changeable decrease. (5) LOI clearly increases. Also, enrichments and depletions of trace elements in hul/cpt–rich rhyolithic-rhyodacitic tuffs depend on the ionic substitutions between some elements having similar ionic radii. In general, Ba, Sr, As, Nb, Th, Ni, Hf, Cs, Pb, Ta, U, B, and HREE relatively enriched in hul/cpt–rich facii and Mn, Zr, Co, W, and most of the LREE relatively enriched in non-zeolitic facii in a lithostratigraphic level. The whole rock chemical compositions of Gördes, Demirci and Şaphane pyroclastic rocks and probably some other west Anatolian Miocene basins have been resulted by partly ion-exchange and -selectivity properties of hul/cpt. Generally, alteration of pyroclastic rocks to zeolites has a prominent effect on their chemical composition. Also, the compositions of zeolite (hul/cpt)–rich pyroclastics rocks in west Anatolia address secondary alteration chemistry not primary chemistry of volcanism, particularly for Si, Ca, Na and LOI and also for some trace elements.

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