

GEOCHEMICAL PROPERTIES AND RODINGITIZATION OF DIABASE DYKES CUTTING PERIDOTITES IN YÜKSEKOVA COMPLEX (ÖZALP, VAN - TURKEY)

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ABSTRACT.- In this study, the geology of diabase dykes which cut peridotites of Yüksekova Complex (Özalp, Van, Turkey) and the effects of Ca metasomatism that caused the metamorphism of these peridotites were investigated. Within the light of mineralogical and petrographical studies and geochemical data; it was determined that diabase dykes that cut peridotites in Yüksekova Complex had shown rodingitization in various degrees due to Ca metasomatism. Depending on this metasomatism, Ca-Al-Mg rich silicates were formed. The mineralogy of rodingitized dykes with ophitic texture is composed of diopside, plagioclase, hydrogrossularite, chlorite, epidote and in minor amounts phlogopite, prehnite, apatite, calcite, opaque minerals. Metasomatism caused enrichment of Ca and depletion of SiO₂ in whole rock major oxides of dykes in tholeiitic character. So, dykes were divided into three different subgroups. The first group is formed from high grade rodingitized diabase dykes (~38.0–42.0 wt. % in SiO₂; 19.0–26.0 wt. % in CaO). The grade of rodingitization in diabase dykes forming the second group is relatively low (~42.5–43.0 wt. % in SiO₂; 14.5–15.0 wt. % in CaO). However, the effect of rodingitization has not been encountered due to results of both petrographical and geochemical analyses in diabase dykes which form the third group (~47.0–50.0 wt. % in SiO₂; 10.0–12.0 wt. % in CaO). It is considered that in rodingitized dykes of which are enriched by trace and REE (Rare Earth Element) contents, the fluids affecting the metasomatic source have developed as a result of interactions with other rocks which were enriched more in these elements. It is also contemplated that the local geology, tectonical structure of the environment and the heat, oxygen fugacity and chemical composition in fluids which would develop due to those factors are significant in this interaction.

Key words: Diabase dykes, peridotite, Ca-metasomatism, element mobility, Yüksekova Complex.

INTRODUCTION

The major oxide trace and REE (rare earth element) contents of ultramafic and mafic rocks of the oceanic lithosphere supply significant contributions in interpreting the geodynamical environments which these rocks have formed (Pearce et al., 1981; Shervais, 2001; Pearce and Stern, 2006). However, the overthrust of ophiolites onto the continent following the intraoceanic imbrication, overthrust processes and long geological evolution which these had been sub-

jected until they took their recent position caused change over the geochemical compositions of these rocks (Coleman, 1977; Puga et al., 1999; Bach and Klein, 2009; Putnis and Austrheim, 2010).

Rodingitization is another phenomenon that causes the metamorphism of rocks of the oceanic crust. Ca rich fluids coming out of pyroxenes during the serpentinization process of peridotites can not enter the structure of serpentine mineral lattices. So; this metamorphism de-

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velops by the Ca metasomatism which these fluids have formed together with serpentinites and other contact rocks (Frost and Beard, 2007; Koutsovitis et al., 2008; Austrheim and Prestvik, 2008). Diopside is one of the most significant minerals supplying Ca addition in fluids forming the rodingitization (Coleman, 1967; Frost and Beard, 2007). The presence of diopside, chlorite and hydrogrossularite minerals which can be defined petrographically in basaltic rocks indicate the presence of rodingitization in these rocks (Tisikouras et al., 2009). Silica activities of fluids that have been derived from the serpentinization of calcic pyroxenes to be low is considered as a reason of increasing CaO wt. % versus depleted SiO₂ wt. % (Li et al., 2008; Bach and Klein, 2009).

The effects of metasomatic events and different alteration processes can partially be revealed by the investigation of major oxide, trace element and REE behaviors. In addition, reliable petrological interpretations could only be made by dwelling on elements which have not relatively been affected during all these processes (Floyd and Winchester, 1975; Pearce and Norry, 1979; Wood, 1980; Pearce, 1982).

The purpose of this article is to investigate the geochemical properties of diabase dykes cutting peridotite deposit in ophiolitic slices located Özalp region, Van, Turkey. It was also aimed at studying metamorphic processes due to rodingitization and analyzing their effects on rock chemistry comparing with dolerite and rodingite samples of Othrys ophiolite.

GENERAL GEOLOGY

Rock assemblages formed by ophiolite and ophiolitic melanges cover large areas in Anatolia (Figure 1-A). As related with the evolution of Paleotethys and Neotethys Oceans, ophiolites are generally observed in areas associated with su-

ture zones in Anatolia which was formed from a couple of microcontinents and separated by these suture zones at different ages (Şengör and Yılmaz, 1981).

Anatolia was divided into tectonical units in east west directions as related with Tethys evolution. Whilst these tectonical units were defined as Pontides, Sakarya Continent, Anatolide-Tauride Block and Southeast Anatolian Fold Belt by Şengör and Yılmaz (1981), these units were classified by Okan and Tüysüz (1999) as Pontides, Anatolide-Tauride Block and as the Kırşehir Massif which is in between them. To which tectonic block the Eastern Anatolia belongs consists of some differences in previous studies. Okan and Tüysüz (1999) included the Eastern Anatolia and the east of Lake Van into Anatolide-Tauride Block. However, Dilek (2008) and Dilek and Furnes (2009) defined the region as Mesozoic continental margin and included it into Pontides. Çakır (2009) claimed the presence of only one Tethys Ocean in Anatolia, interpreted that the south of the Neotethyan suture zone which had passed through the southern boundary of Pontides as Arabian Promontory (this area also covers the Lake Van and its eastern part).

However, Şengör et al. (2003), Keskin (2005) and Şengör et al. (2008) defined the region where our study area is also located in as an “accretional mélangé”, as the “East Anatolian Accretional Complex” (EAAC) that developed on the Neotethyan oceanic lithosphere subducting under Eurasian continent towards north in Upper Cretaceous – Oligocene periods. This complex is observed as a belt trending in NW-SE in 150-180 km width. It was also stated that EAAC which reflects the connection of pieces of continental and oceanic crusts between the Arabian and Eurasian plates got into domal shape and elevated 2 km during the collisional stage which started in Mid Eocene and even continues today

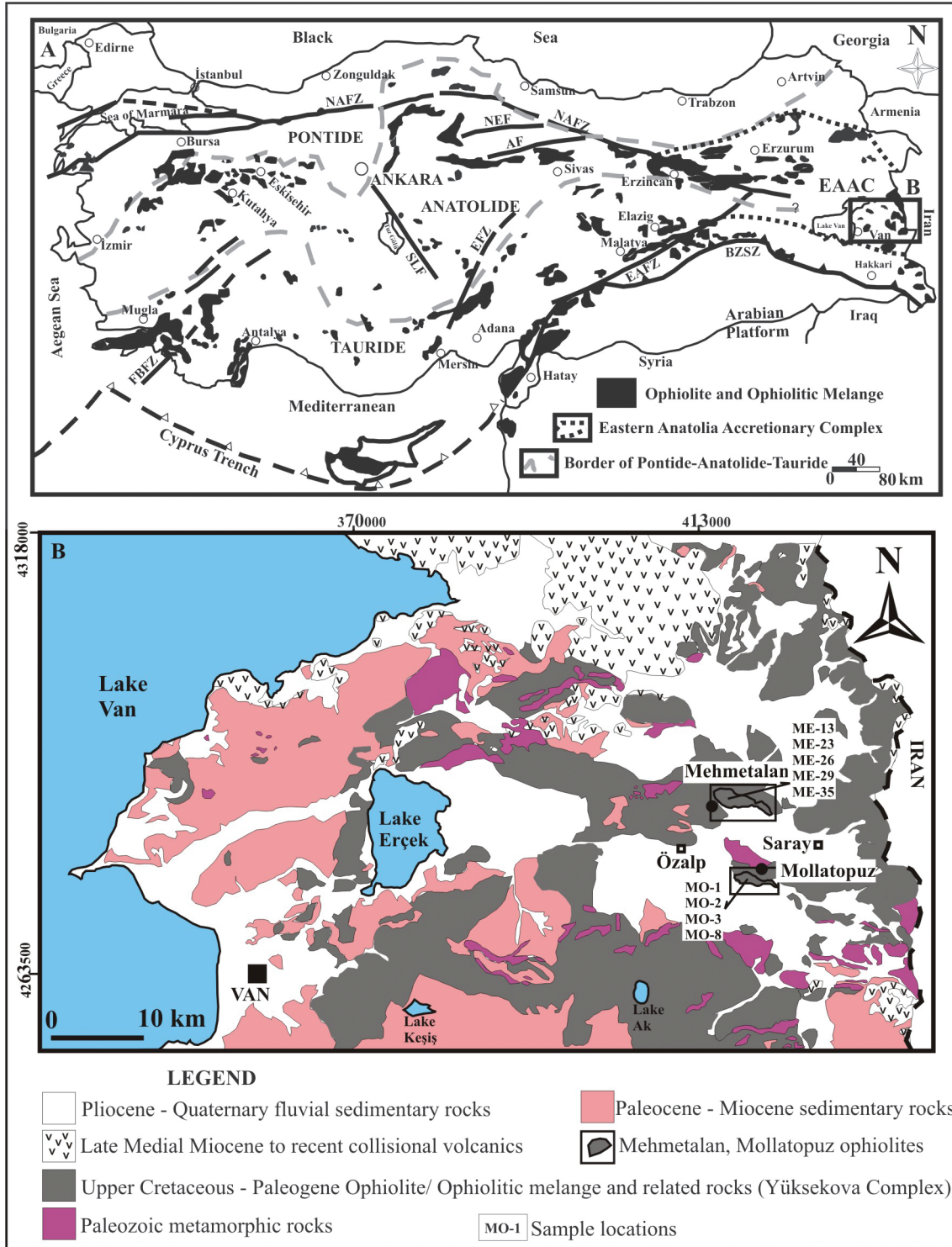


Figure 1- A Distribution of ophiolites in Anatolia (the boundary of tectonic units (Okan and Tüysüz, 1999), the distribution of ophiolites (Uçurum et al., 2006) and the boundary of dyke (Keskin, 2005); B) Geological map of the region between Eastern side of Lake Van and Iranian Border (modified from Şenel, 2002).

(Elitok and Dolmaz, 2007; Yılmaz, 1993; Bozkurt, 2001; Koçyiğit et al., 2001; Barazangi et al., 2006, Şengör et al., 2008).

The south and east of EAAC is covered by ophiolitic units deposited in Late Paleocene aged flyschoidal sequences from Upper Oligocene to Pliocene (Şengör et al. 2003) and by post Oligocene young sediments. Paleozoic aged metamorphic blocks are observed as dispersed and at different positions with these blocks. These metamorphic blocks are assessed as pieces of Anatolide-Tauride microcontinents (Göncüoğlu et al., 1997; Okay and Tüysüz, 1999). It is known that the flysch becomes younger, its surround gets shallower from Cretaceous to Oligocene and Oligocene aged units at north become an unconformable cover going from north to south through complex (Tüysüz and Erler, 1993).

However; volcanic units are observed in north and northeastern parts of the accretional complex. Ophiolitic layers located in EAAC represent pieces of the Neotethyan oceanic lithosphere that lasted from Triassic to Miocene over the region (Şengör and Yılmaz, 1981; Robertson and Dixon, 1984; Ustaömer and Robertson, 1997). Ophiolitic units of the Özalp Region are observed in the form of slices approximately in east-west directions within accretional complex (Figure 1-B). These ophiolitic units are generally represented by peridotite, gabbro and by sporadically cutting rodingitized diabase dykes.

Peridotites represented by tectonic textured harzburgites in Özalp Ophiolites generally extend in EW directions. Diabase dykes forming the subject of the study are almost fragmented and show an approximate parallelism to the EW extension (Figure 2). Partly preserved dykes which are 1 to 2 meters in thickness and 30 to 40 meters in length are rarely observed over these regions. Isolated diabase dykes are brownish and outer surfaces are pale yellowish at rodingitized sections. These dykes over their broken fresh

surfaces are seen in color tones ranging from black to gray and have porphyritic texture (Figure 2a).

Mafic dykes are more resistant than peridotites. During upwelling because of its resistance, these have caused the development of weak zones with accompanying peridotites along the contact. Boudinaged dykes are observed as surrounded by a serpentinized belt which had occasionally reached 1 meter in thickness and developed along weak zones. These dykes have more intensely serpentinized periphery than peridotites that accompany them along boudin axes (Figure 2 b, c). Along these serpentinized belts, foliations which their elongations have approximately developed parallel to the elongation of boudins are seen.

The alteration which was detected petrographically in isolated dykes (uralitization, formation of chlorite, epidote) shows that these overall dykes could be defined as diabase. Rodingitization is more effective in dykes which are observed by its boudinaged structures. These dykes have gained a schistose structure by its yellowish color tone and occasional shearing in them. It is assumed that rodingitized dykes that were situated with peridotite units had gained its boudin structure during internal shear along the period starting from the formation of accretional melange to its recent position (Cawood et al., 2009).

METHOD OF STUDY

Total of 50 samples were collected from dykes observed in ophiolitic slices cropping out at northeast and southeast of Özalp County located at east of Lake Van. After these samples had petrographically been studied, 9 thin sections were prepared to perform geochemical analyses in the Thin Section Laboratory of the Geological Engineering Department at Yüzüncü Yıl University in Van, Turkey. Major oxide, trace element and REE contents of samples prepared

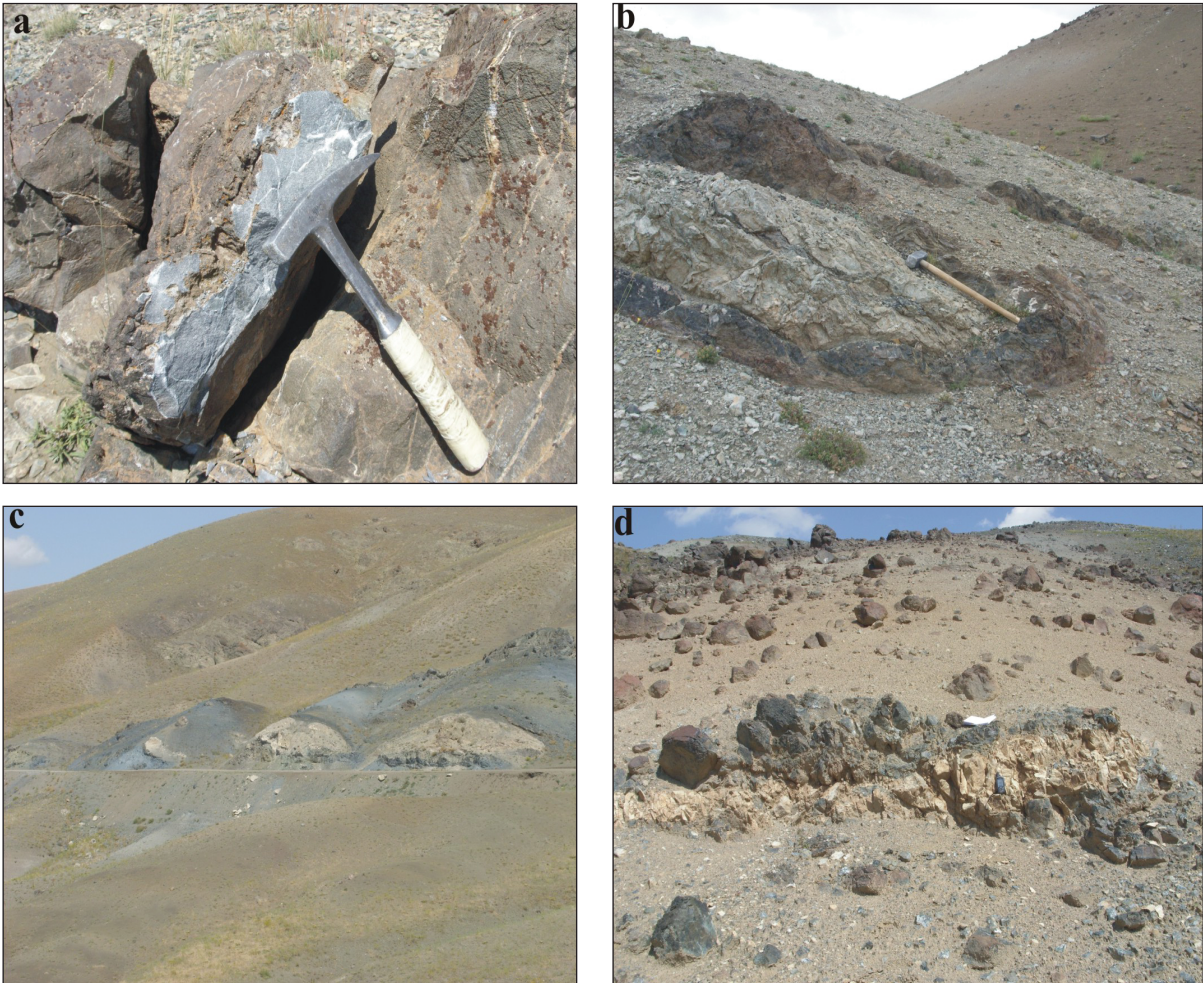


Figure 2- a) A view from fresh diabase dyke surfaces, b) diabase dyke observed in a folded structure, c) a view from diabase dykes that have gained boudin structure, d) a view of rodingitized linear diabase dyke.

were analyzed by ICP – AES / ICP – MS (Inductively Coupled Plasma – Atomic Emission Spectrometry / Mass Spectrometry) methods at ALS laboratories in Canada. In order to confirm some mineral assemblages defined at petrographical studies, XRD (X-Ray Diffraction) and mineral description analyses were also carried out for samples MO-1 and ME-23 in MTA (General Directorate of Mineral Research and Exploration) in Ankara, Turkey.

PETROGRAPHY AND MINERALOGY

Diabase dykes cutting peridotites were par-

tially rodingitized by Ca metasomatism in ophiolitic slices of the Özalp region (Figure 3, a, b). These mafic dykes typically exhibit ophitic texture in thin sections. The rock is mainly composed of uralitized clinopyroxene (diopside), plagioclase, garnet (hydrogarnet), chlorite, epidote, phlogopite, apatite, calcite and of opaque minerals. Although most of dykes are seen as rodingitized in thin sections, partly fresh dolerite dykes were observed as well (Figure 3 c, d).

Pyroxenes among prismatic plagioclase crystals are represented by diopside and augite.

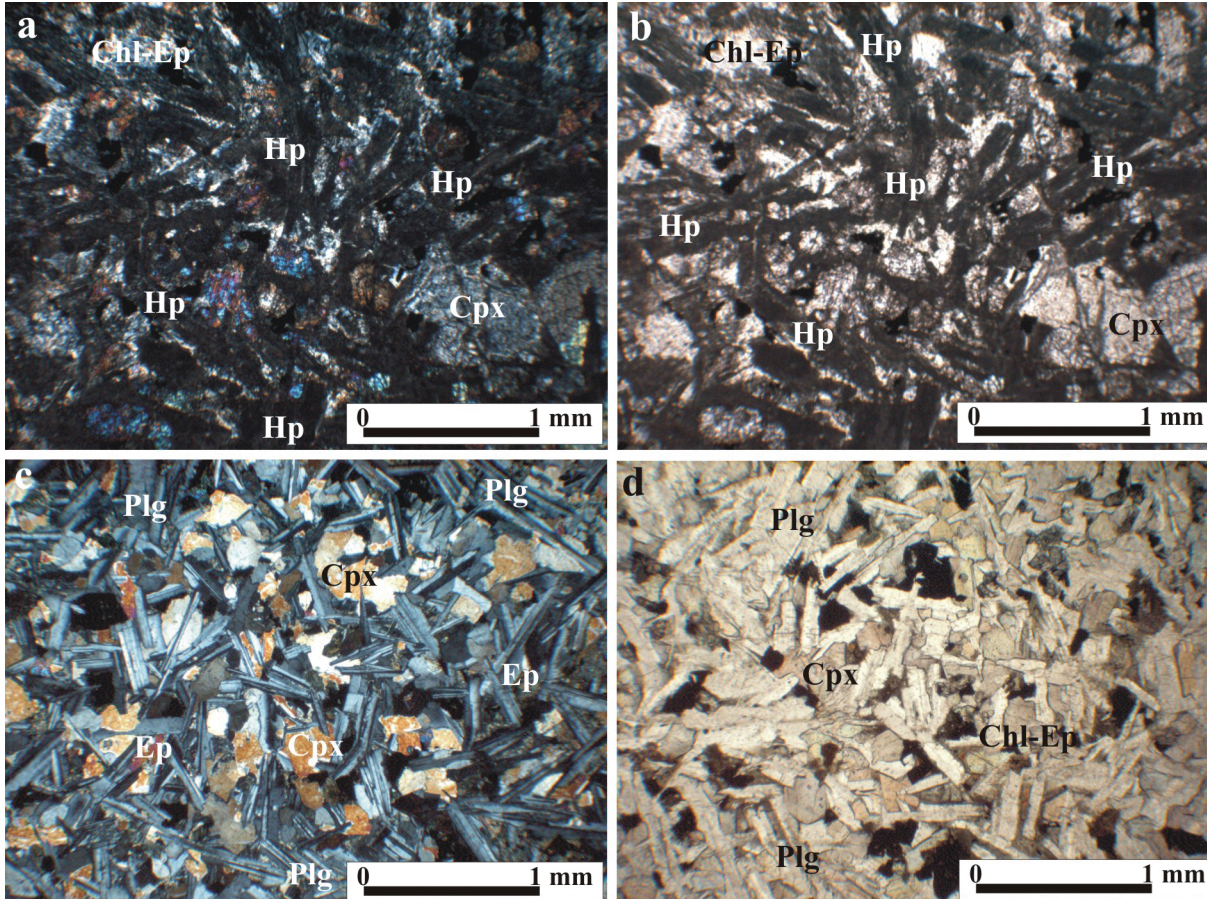


Figure 3- Thin section views of diabase dykes (a, c: crossed nikol; b, d: parallel nikol), (a-b) rodingitized diabase dykes, sample no: ME-23; (c-d) dolerite dyke sample no: MO-8, (Plg: plagioclase, Cpx: Clinopyroxene, Ep: Epidote, Hp: Hydrogrossularite, Chl-Ep: Chlorite-Epidote).

Uralitization and chloritization were frequently encountered in pyroxene phenocrystals. Hydrogarnet and sericite being formed from plagioclases form the most frequently observed metasomatism and alteration minerals. Subhedral opaque minerals were detected in all thin sections in addition to apatites found as accessory mineral. The assemblage of calcite, titanite, actinolite, chlorite and epidote which were especially observed in some thin sections are seen as an indicator of low grade hydrothermal alteration within greenschist facies (Elthon, 1979; Spear, 1981). Petrographical observations indi-

cate that rodingitization periods developed on dykes could be classified according to the relative abundance of hydrogrossularite in thin sections.

Petrographically defined diopside, chlorite and hydrogrossularite mineral assemblages in dykes of Özalp ophiolites indicate the petrographical data of rodingitization in these dykes (Tisikouras et al., 2009). The presence of this mineral assemblage detected in petrographical studies was also verified by XRD analyses (Figure 4).

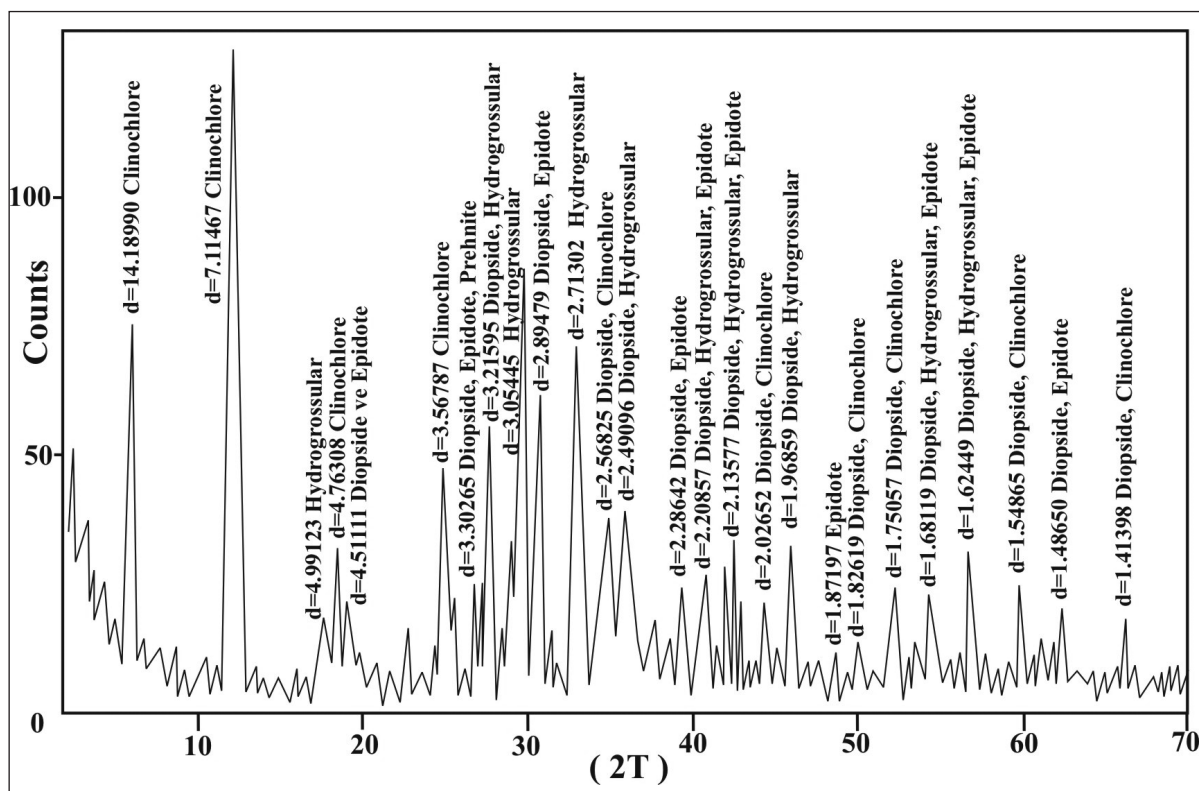


Figure 4- Simplified XRD chart of the rodingitized sample MO-1.

GEOCHEMISTRY

Results of major oxide, trace and REE analyses of dyke samples taken from Özalp ophiolites are given in table 1. In addition to samples which the effect of alteration was intensely observed, ME-29 from Mehmetalan field and MO-8 from Mollatopuz field showed an alteration effect at a lower grade than other samples. Weight loss values due to heat in these samples are 2.5 and 3.46 wt. % for ME-29 and MO-8, respectively. Weight loss values due to heat of the other samples vary between 4.25 – 6.34 wt. %. Generally; these heat weight loss values are the indicator of low grade hydrothermal alteration.

For the geochemical classification of these dykes the elements which are considered as un-

affected were relatively used, because of the alteration effect detected in petrographical studies (Figure 5). Dolerite and rodingite samples of the Othrys ophiolite seen in diagrams were used in order to emphasize on the similarities of major geochemical characteristics with the samples used in this study. Dykes fall into subalkaline basalt field in $Zr/TiO_2 \cdot 0.0001$ vs Nb/Y diagram (Winchester and Floyd, 1977), which is reliably used in the classification of basaltic rocks that affected from alteration (Figure 5a).

Toleitic basalts are distinguished from alkaline basalts with their relatively low P_2O_5 content (Winchester and Floyd, 1977). Tholeiitic and alkaline basalts which exhibit the behavior of an incompatible element in magmatic differentiation

Table 1- Geochemical analysis results of dykes in Mehmetalan and Mollatopuz fields. HGRD- high grade rodingitized diabase dykes, LGRD- low grade rodingitized diabase dykes, DD- unrodingitized diabase dykes. Major and trace elements are in % and ppm, respectively (Othrys dolerite and rodingite samples were taken from Koutsovisit et al., 2008; Tsikouras et al., 2009).

	Diabase and rodingite in the study										Dolerite and rodingite of Othrys ophiolite							
	HGRD					LGRD		DD			Dolerit			Rodengit				
	ME-13	ME-23	MO-1	MO-2	MO-3	ME-26	ME-35	MO-8	ME-29	OD-1	OD-2	OD-1	OR-1	OR-2	OR-3	OR-4		
SiO ₂	38,2	39	37,9	39,1	41,8	42,5	43,1	49,6	47,1	59,17	58,78	53,91	41,49	39,59	38,94	38,89		
Al ₂ O ₃	12,75	14,75	13,7	13,1	13,25	17,65	15,3	14,55	15,05	14,81	14,68	15,41	10,68	10,89	12,81	17,27		
Fe ₂ O ₃	9,01	9,18	8,95	9,53	9,7	8,09	9,25	10,8	11,8	10,47	9,3	8,32	7,41	10,73	9	9,62		
CaO	19,3	20,2	24,8	23,2	20,4	15,05	14,6	11,6	10,2	8,46	8,01	5,74	19,53	17,21	21,93	16,38		
MgO	9,03	8,5	6,19	6,43	6,2	8,36	9,13	5,34	6,98	3,35	3,73	8,13	16,22	14,73	11,19	11,52		
Na ₂ O	3,1	1,89	1,62	1,74	2,04	2,56	2,63	2,85	3,78	1,54	2,14	5,23	0,01	0,11	0,09	0,03		
K ₂ O	0,01	0,02	0,02	0,04	0,1	0,18	0,29	0,93	0,45	0,1	0,2	0,05	0,04	0,04				
TiO ₂	0,87	0,91	1,03	1,12	1,16	0,75	0,9	0,59	1,41	0,48	0,46	0,26	0,23	1,16	0,92	0,46		
MnO	0,15	0,16	0,15	0,16	0,17	0,14	0,16	0,16	0,2	0,13	0,14	0,17	0,17	0,31	0,27	0,23		
P ₂ O ₅	0,07	0,09	0,09	0,11	0,1	0,07	0,09	0,04	0,14	0,05	0,04	0,02	0,02	0,06	0,05	0,03		
LOI	6,34	5,51	5,52	5,53	4,86	4,25	4,66	3,46	2,5	0,79	2,48	2,8	5,1	5,13	4,72	5,8		
Total	98,9	100,5	100	100	100	99,8	101	100,5	99,8	99,35	99,96	100	100,89	100,01	99,92	100,23		
Co	46,6	44,7	36,4	38,6	37,7	43,5	47,5	37,5	45,6	30	27			53	39			
Cr	420	370	210	220	200	350	400	70	190	30	20	84	1528	600	420	312		
Ni	196	165	90	94	81	169	192	42	80	20	30	47	459	220	150	84		
Ba	20,8	27,6	16,7	31,4	66,1	747	1135	70	689	9	16	4,5	15,1			6		
Rb	1,2	1,5	0,5	1,6	2,7	3,6	6,9	11,6	9,4		4							
Sr	204	181	142,5	614	2610	579	520	270	424	78	139	157,2	3,4			20,5		
Th	0,4	0,43	0,47	0,5	0,54	0,39	0,43	0,32	0,88	0,36	0,39	0,3		0,08	0,06			
Ta	0,1	0,2	0,2	0,2	0,2	0,1	0,1	0,1	0,3	0,06	0,05	0,1		0,04		0,1		
Nb	2,6	2,7	3,2	3,5	3,7	2,2	2,7	1,9	4,8	1	0,9			0,6	0,5	1		
Hf	1,6	1,7	1,9	2	2,2	1,4	1,7	1	2,7	0,8	0,8			1,7	1,4	0,7		
Y	20,9	21,8	23,7	25,3	26,8	17,9	21,9	17,6	32,8	12	13,5	5,8	8,3	28,3	24,1	11		
Zr	57	59	65	71	74	48	59	29	97	19	22	6,9	6,1	41	35	18,1		
La	4,3	4,4	4,8	5,2	5,4	4,5	4,6	2,6	7,7	1,41	1,53	0,7	0,6	1,18	1,05	0,8		
Ce	10,4	10,8	11,7	12,6	13,3	10,4	11	5,7	18,4	3,52	3,84	1,8	0,7	4,23	3,75	2		
Pr	1,46	1,51	1,63	1,74	1,84	1,37	1,53	0,75	2,56	0,47	0,51	0,2	0,12	0,85	0,75	0,32		
Nd	7,2	7,6	8,2	8,7	9,3	7	7,8	4	12,5	2,52	2,73	1,1	0,6	5,79	5,1	2		
Sm	2,33	2,42	2,73	2,75	2,96	2,08	2,39	1,33	3,78	0,81	0,92	0,2	0,3	2,41	2,13	0,8		
Eu	0,95	0,95	1,09	1,07	1,15	0,85	1,01	0,56	1,47	0,371	0,402	0,15	0,1	2,19	3,45	0,26		
Gd	2,85	2,92	3,17	3,37	3,59	2,56	3	1,87	4,51	1,24	1,37	0,6	0,75	3,55	3,08	1,22		
Tb	0,52	0,54	0,6	0,62	0,67	0,47	0,55	0,39	0,85	0,27	0,3	0,12	0,18	0,75	0,63	0,27		
Dy	3,46	3,64	3,95	4,12	4,41	3,01	3,63	2,73	5,46	1,92	2,23	0,92	1,21	4,92	4,1	1,74		
Ho	0,77	0,83	0,88	0,94	0,98	0,65	0,82	0,63	1,23	0,43	0,47	0,19	0,28	0,99	0,84	0,39		
Er	2,28	2,43	2,7	2,8	3	2,01	2,42	2,01	3,71	1,4	1,51	0,64	0,94	2,94	2,48	1,21		
Tm	0,34	0,37	0,37	0,42	0,42	0,29	0,35	0,31	0,55	0,226	0,239	0,09	0,17	0,433	0,365	0,19		
Yb	2,22	2,28	2,51	2,66	2,79	1,86	2,33	2,09	3,55	1,57	1,63	0,77	1,14	2,72	2,33	1,36		
Lu	0,33	0,36	0,37	0,42	0,44	0,29	0,36	0,31	0,54	0,262	0,265	0,13	0,16	0,411	0,354	0,22		

by these properties can be divided into two different areas with respect to Zr. It is seen that low P_2O_5 (0.04-0.14) contents and diabase dykes of Özalp ophiolite slices fall into the Tholeiitic field (Figure 5 b). It is seen in diagrams that, dolerite and rodingite samples of Otrhys ophiolite are in tholeiitic character.

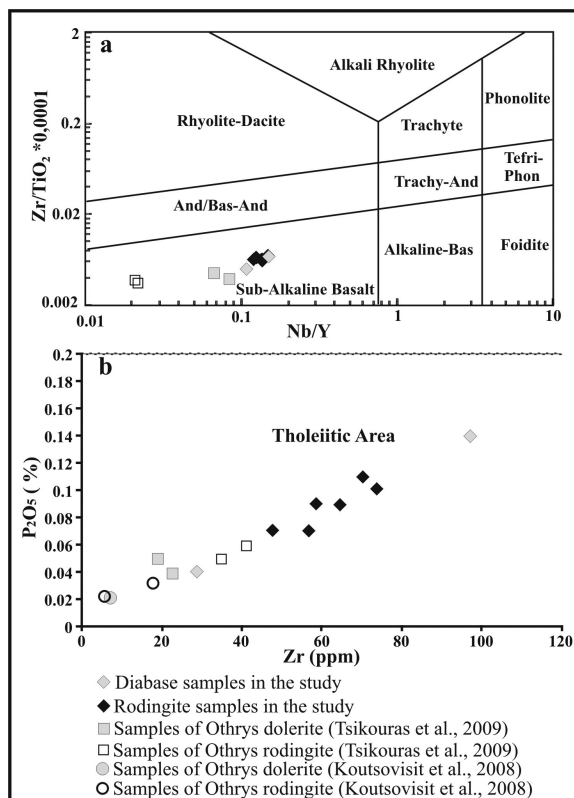


Figure 5- a) Zr/TiO_2 vs Nb/Y classification diagram (Winchester and Floyd, 1977), b) P_2O_5 / Zr classification diagram (Winchester and Floyd, 1976).

DISCUSSION

Dykes which constitute the subject of this study are tholeiitic in character and were divided into three different subgroups according to the results geochemical analyses, also in compliance with petrographical observations. The first group is the “high grade rodingitized diabase dykes” and has 41.8 – 37.9 wt. % SiO_2 and 19.3 – 25.7

wt. % CaO. The second group is the “low grade rodingitized diabase dykes” that has 42.5-43.1 wt. % SiO_2 and 14.55-15.05 wt. % CaO. However, the diabase dykes that have no effect of rodingitization constitute the third group. There was not encountered rodingitization in this group neither in petrographical nor in geochemical analysis results. Although diabase dykes forming this group have 47.1-49.6 wt. % SiO_2 , the weight % values for CaO range in between 10.2 – 11.6. On the ternary diagram, prepared by the correlation of changes on rodingitization duration and major oxide elements, it was seen that the high grade rodingitized samples cumulated in rodingitized areas (Figure 6). Unrodingitized samples cumulate farther from high grade rodingitization field than low grade rodingitized samples.

Rodingites indicate the presence of metasomatic events at low temperatures which were affected by fluids originating from the serpentinization of peridotites (Coleman, 1967; Dubinska, 1995 and 1997; Normand and Williams-Jones, 2007). The effects of these metasomatic events become evident with the enrichment of wt. % in CaO (~25.7) but a depletion in the wt. % in SiO_2 (~37.9) in whole rock geochemistry's. The increase in the CaO ratio in dykes of Özalp ophiolite requires the supply of Ca addition to the source of rodingitization. Fluids at low temperatures resulting with serpentinization are characterized by being alkaline (generally $pH > 10$) and enriched by Ca (Palandri and Reed, 2004). It is considered that Ca addition to metasomatic source could only be made by the serpentinization of calcic pyroxenes. Diopside is one of the most important minerals that could supply Ca addition to the source of rodingitization (<http://webmineral.com/data/Diopside.shtml>) with its total oxide ratio $[CaMg(Si_2O_6)]$ 25.90 % CaO – 18.61 % MgO and 55.49 % SiO_2 (Coleman, 1967; Austrheim and Prestvik, 2008). Serpentinization process of diopside might occur by the reaction given below by Frost and Beard (2007).

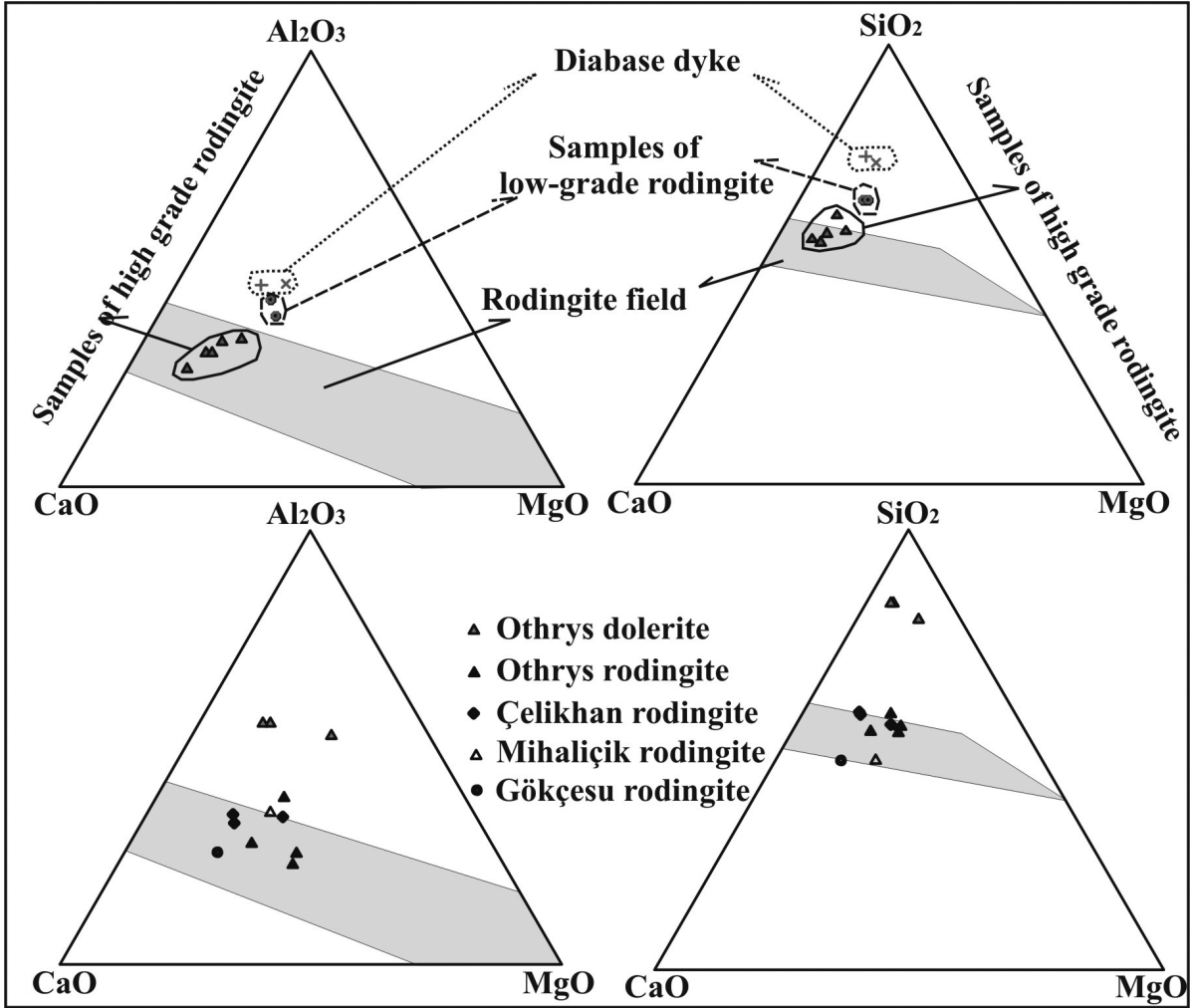
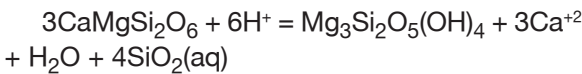


Figure 6- Ternary diagram of major oxides in which rodingitization areas are shown (each areas were taken from different authors as; rodingitization areas (Frost and Beard, 2007); Mihaliçik rodingite samples (Çoğulu and Vuagnat, 1965); Çelikhan rodingite samples (Pişkin, 1975); Gökçesu rodingite samples (Bassaget et al., 1967); Othrys dolerite and rodingite samples (Koutsovisit et al., (2008) and Tsikouras et al., (2009)).



Serpentinization and the Ca^+ addition to the source in this equilibrium which developed as a reaction of diopside with H^+ in fluids are clearly seen. Moreover; as the alkalinity increases in fluids along the overall reaction, the silica activity rapidly decreases. One of the significant reactions that decrease the silica activity in fluids is the serpentinization and talc occurrence

processes of Mg silicates in these environments (Frost and Beard, 2007). The Ca increase in metasomatic source supplying the rodingitization occurs with the degradation of calcic pyroxenes in serpentinization process. However; silica % values of diabase dykes which rodingitization effects were not observed are higher than low and high grade rodingitized dykes (see Table 1, Figure 7). This phenomenon is the indicator of depleted SiO_2 in the source of rodingitization. The low amount in silica activities of fluids which

derived from the serpentinization of calcic pyroxenes is interpreted as the reason of SiO₂ depletion at the source of rodingitization (Frost and Beard, 2007; Li et al., 2008; Bach and Klein, 2009). Hence; rodingitization phenomenon being realized by the Ca metasomatism in dykes of Özalp ophiolites is verified by CaO enrichment in whole rock geochemistry results. However, this case reveals the reason of the depletion of SiO₂ in dykes.

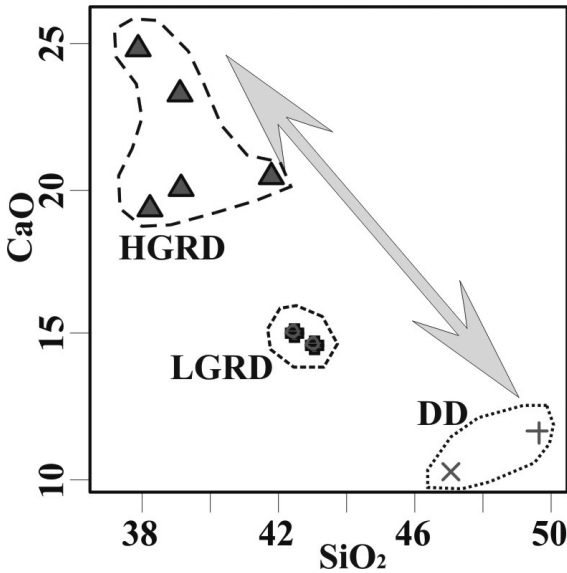
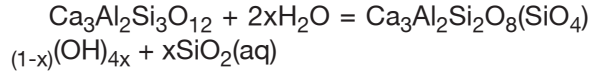
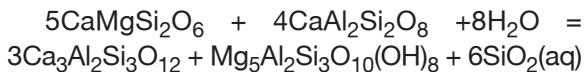


Figure 7- CaO-SiO₂ Harker diagram of the isolated diabase dykes (HGRD: high grade rodingitized dykes; LGRD: low grade rodingitized dykes; DD: unrodingitized diabase dykes).

Hydrogrossularite and chlorite which are the characteristic minerals of rodingites occur as the secondary product due to the reaction of Ca-Mg silicates with calcic plagioclases during reaction processes developed by the effect of fluids over the source of rodingitization. Typical reactions of these processes were explained below by Frost and Beard (2007).



Geochemical properties of samples indicate that all reaction pairs presented within the availability of minerals that developed as a result of rodingitization had occurred in dykes of Özalp ophiolite.

Normalized MORB multi element spider diagrams of isolated dykes were presented in figure 8. In multi element spider diagrams which is prepared by normalizing to MORB, trace element contents of dykes are seen as it had been more enriched with respect to Mid Oceanic Ridge Basalts (MORB) by Large Ion Lithophile (LIL) elements (LIL- Cs, Rb, K, Ba, Sr). As LIL elements show various distributions, the depletion in Nb is encountered despite the enrichment in Th element. However; there is observed parallel but partly depleted distribution to normalized MORB line in High Field Strength (HFS) elements in this diagram (such as; Zr, Sm, Ti, Y, Yb). It is seen that value ranges of diabase and rodingite dykes of Mehmetalan and Mollatopuz show a consistent distribution except for LIL elements. Yet;

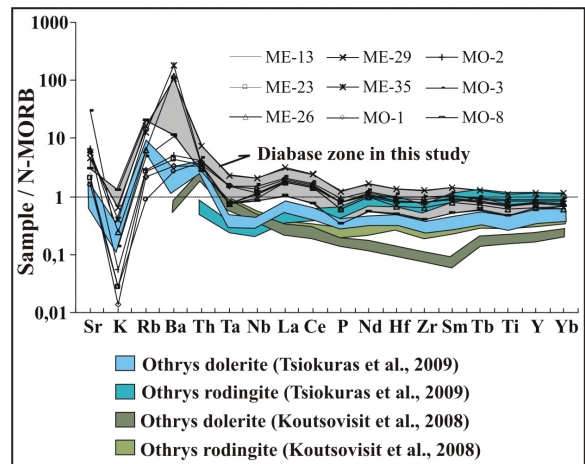


Figure 8- Multi element spider diagrams of isolated dykes normalized to MORB (normalized MORB values were taken from Sun and Mc Donough, 1989).

clear differences are observed among Othrys dolerite and rodingite samples. Despite Th depletion in Othrys rodingites, there is not observed an evident difference in Ta, Nb, La and Ce elements but enrichment in all HFS elements starting from element P. This case is also valid for the other samples taken from various sites of Othrys ophiolite (Koutsovisit et al., 2008).

Element mobility is controlled by mineralogical changes that occur during alterations. It is known that alkali elements have high mobility due to alteration processes. At time of low grade alteration and metamorphism, studies carried out on behavior of elements showed that some of them were depleted or enriched, while of some remained as stable (Cann, 1970; Coish, 1977; Humpris and Thompson, 1978). The irregular distribution of Ba, Sr, Rb, and K elements in the multi element spider diagram (normalized to MORB) of isolated dykes may reflect the effect of alteration and/or metasomatic events. It is also known that these elements are rather mobile under metamorphic conditions due to low ionic potentials (< 3) (Pearce and Cann, 1973; Pearce, 1975, 1982, 1983; Saunders et al., 1980). It is claimed that Th element are stable even under conditions of alteration, sea bottom metamorphism and greenschist metamorphism as it has high ionic potential ($3 <$) (Pearce, 1975, 1983; Wood, 1980). In addition to the decrease from Th to Nb which shows enrichment above the normalized MORB line in isolated dolerite dykes, values beneath the line of normalized MORB in HFS elements might reflect the effect of component of subduction zone (Pearce and Stern, 2006). Ta and Nb in the spider diagram are the elements that have the highest ionic potentials (7). However, it is seen that value ranges of Ta and Nb elements have not been subjected to significant changes in dolerite and rodingite samples. There is observed a significant enrichment from Ce to Yb only in Othrys rodingites, although they have high ionic potential ($3 <$) compared to dolerites. It is difficult to say that

this situation has developed by the effect of alkali fluids only in metasomatic source, since such a case was not observed in rodingite samples during the study. Therefore; it seems probable that the enrichment of the metasomatic source of Othrys rodingites by fluids interacted with alkaline rocks. There is observed a similarity in REE distribution patterns between the rodingitized diabase dyke samples and unrodingitized dyke samples in REE spider diagram normalized to Chondrite (Figure 9). Especially; a slight enrichment in Light Rare Earth Elements (LREE: La, Ce, Pr, Nd, Pm, Sm) relative to Heavy Rare Earth Elements (HREE: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) is one of most important data exhibiting the difference of magmatic source of dykes than MORB in the study. Despite that; it was seen that Othrys dolerite samples had been enriched by HREE relative to LREE. This situation indicates that Othrys dolerites could be derived from the partial melting of a MORB source at high temperatures at shallow depths.

Rodingitized samples in REE contents of dykes in this study take place within the value ranges of samples MO-8 and ME-29 which the effect of rodingitization effect was not observed. However, looking at REE distributions of dolerite and rodingite samples taken from different areas of Othrys ophiolite, it is observed that REE contents of rodingite samples show a more obvious enrichment trend except for La and Ce elements compared to dolerite samples (Koutsovisit et al., 2008; Tsikouras et al., 2009). Unless fluid/rock ratios of REEs are very high under low grade metamorphic conditions, they are accepted as immobile compared to trace elements (Michard, 1989). In addition to this, much altered rocks which were subjected to high grade metamorphism are not totally immobile, either (Humphries, 1984). The positive Eu anomaly in Othrys rodingite samples (Tsikouras et al., 2009) indicate the degradation of feldspar minerals enriched by Eu within the presence of early differentiation fluids (Hopf, 1993). According to the results of geo-

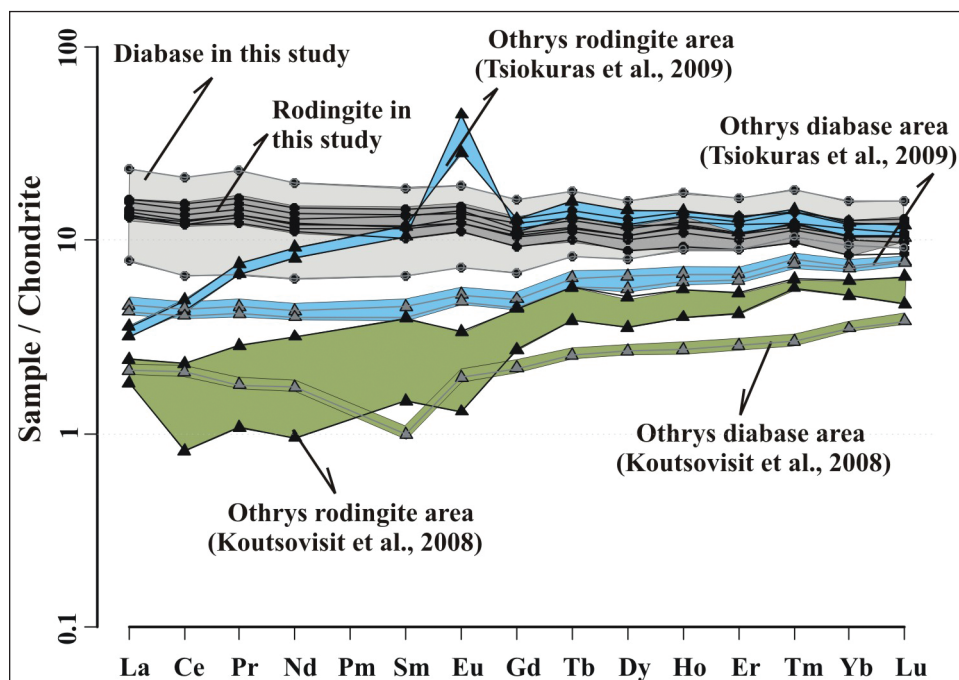


Figure 9- REE diagrams of isolated dykes normalized to Chondrite (REE normalization values were taken from Sun and McDonough (1989)).

chemical analyses, the values of Othrys dolerites [~ 59 wt. % SiO_2 - ~ 8 wt. % CaO - ~ 3 wt. % MgO - ~ 14 wt. % Al_2O_3 (Tsiokuras et al., 2009), ~ 54 wt. % SiO_2 - ~ 5 wt. % CaO - ~ 8 wt. % MgO - ~ 15 wt. % Al_2O_3 (Koutsovisit et al., 2008)] show differences in terms of SiO_2 according to major oxide values of samples in this study (MO-8, 49 wt. % SiO_2 , ME-29, 47 wt. % SiO_2). It can be considered that differences in whole rock chemistry over the source of rodingitization within this value range are effective in post rodingitization REE distributions. However, when rodingitization degree in dykes investigated are generally considered according to SiO_2 and CaO proportions which rodingites contain, REE enrichment at approximate levels in all rodingite samples could be expected to occur. Whereas; REE contents of rodingite samples analyzed in this study exist within value ranges of original rocks. This makes us think that, metasomatic source of Othrys rodingites were enriched by fluids which was interacted with REE enriched alkaline rocks as it was the same as in REE differentiations.

Positive correlations of elements such as; Zr, Y, Ti, Nb observed in ophiolitic mafic rocks are in compatible with olivine-clinopyroxene-plagioclase fractionation (Pearce and Norry, 1979; Pearce, 1982). This situation enables Zr element to be used as a fractionation index. In trace element Harker diagrams of isolated dykes prepared with respect to Zr show disordered trends. This situation forms an alteration effect free of fractionation. However, it can be said that trace elements that exhibit a linear trend were not affected from alteration and metasomatic events (Figure 10). Indeed; the trace element distributions of dykes which were not affected from Ca metasomatism and rodingitized dykes in these diagrams exhibit the same correlations.

Elements such as Th, Ti, Y, Yb, Nb, La, Ce and Lu are frequently used in petrogenetic interpretations especially for ophiolitic mafic rocks (Pearce and Cann, 1973; Winchester and Floyd, 1976; Pearce and Norry, 1979; Wood, 1980;

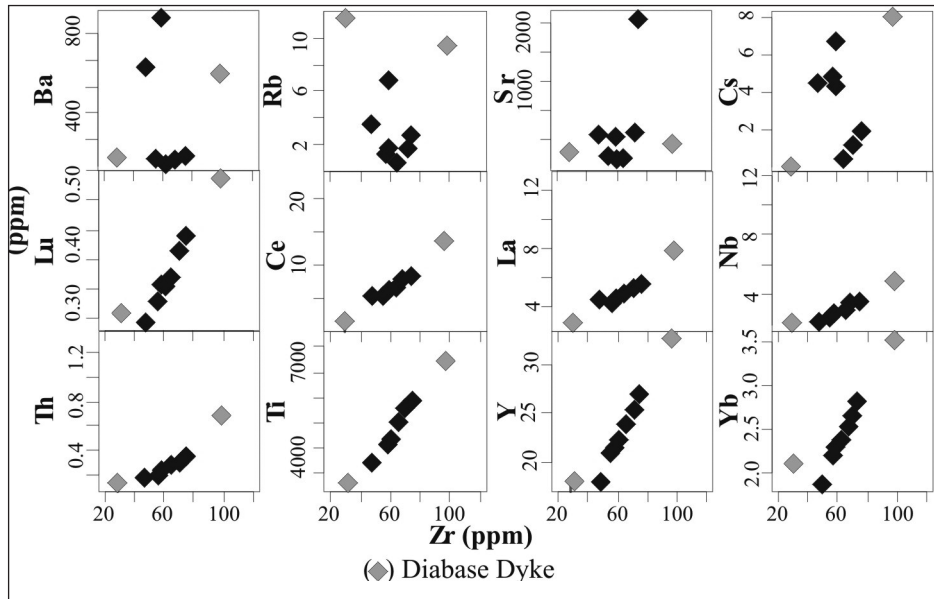


Figure 10- Trace element Harker diagrams prepared with respect to Zr.

Pearce, 1982). It shows that these elements could reliably be used even in the presence of metasomatic effects in dykes of Özalp ophiolites.

The effect of Ca metasomatism on certain major oxide elements were analyzed in the columnar graphic shown in figure 11. The correlations of samples ordered by decreasing SiO_2 values are observed starting from unrodingitized samples in this graph. The determination values (R^2) for SiO_2 (~0.9), CaO (~0.6) and MgO (~0.4) show positive correlations for rodingitization processes. However, R^2 values for Al_2O_3 (~0.05) and Fe_2O_{3T} (~0.07) give quite poor correlations in the graph shown in figure 11. This state might indicate that Al_2O_3 and Fe_2O_{3T} oxides were not relatively affected from rodingitization processes.

It is accepted that transient metals such as Cr, Ni which could enter the lattice of silicate minerals like serpentine and olivine are relatively immobile at low grade alteration (Staudigel et al., 1996). The columnar correlation diagram

which was prepared to assess the behaviors of Co element, one of the transient elements together with Cr and Ni, showed that these elements were quite mobile at metasomatic source (Figure 12).

High positive determination coefficient value (R^2) for Cr (~0.9), Ni (~0.9) and Co (~0.6), ranging from samples in which rodingitization were not observed towards rodingitized samples in this diagram indicate that these transient metals were enriched at metasomatic source.

Element mobility in altered rocks with respect to their original rocks could be analyzed by Isocon analysis. Effectively shown method details of element mobility were explained by Grant (1986). Isocon method is the technique which the enrichment or depletion of elements in altered rocks with respect to original rocks could be revealed even at very minor quantitative values. Gain and loss estimations of rodingitized dykes using this method were represented in table 2. Negative values in this table indicate depletion, however positive values indicate enrichment. Average val-

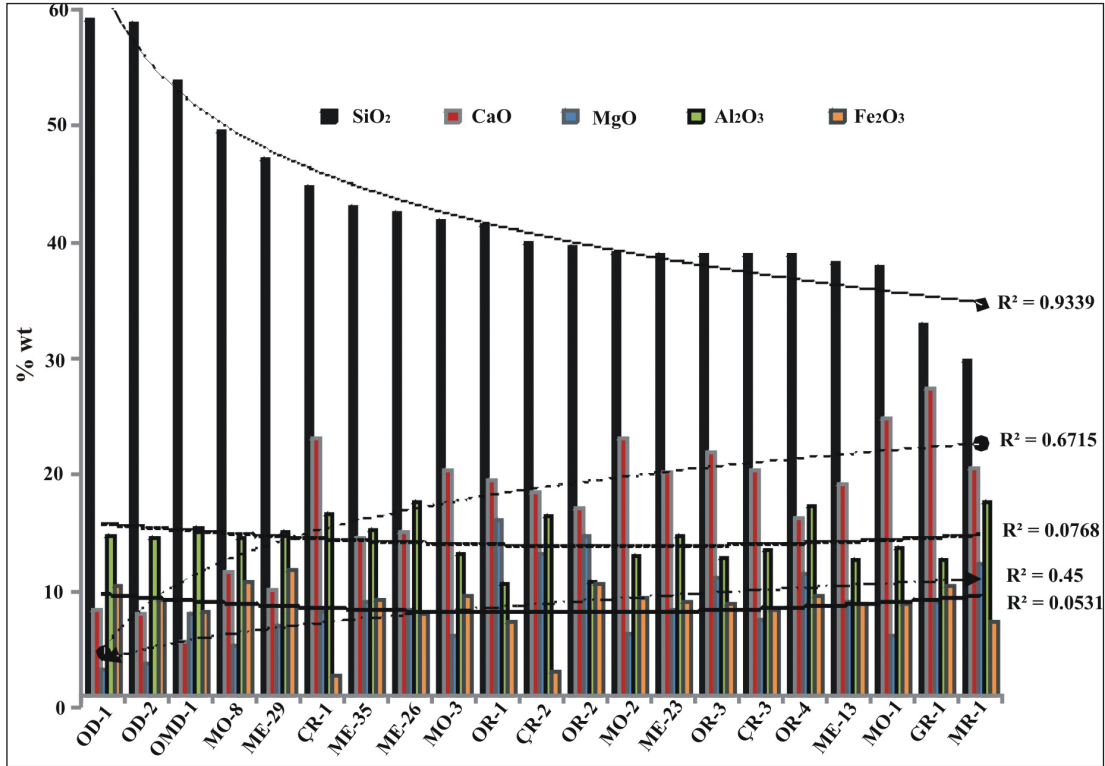


Figure 11- Columnar correlation diagram of major oxide elements. Values of each samples were taken from the related authors (OD-1, OD-2, OR-2, OR-3 (Tsiokuras et al., 2009); OMD-1, OR-1, OR-4 (Koutsovisit et al., 2008); ÇR-1, ÇR-2, ÇR-3 (Pişkin, 1975); GR-1 (Bassaget et al., 1967) and MR-1 (Çoğulu and Vuagnat, 1965).

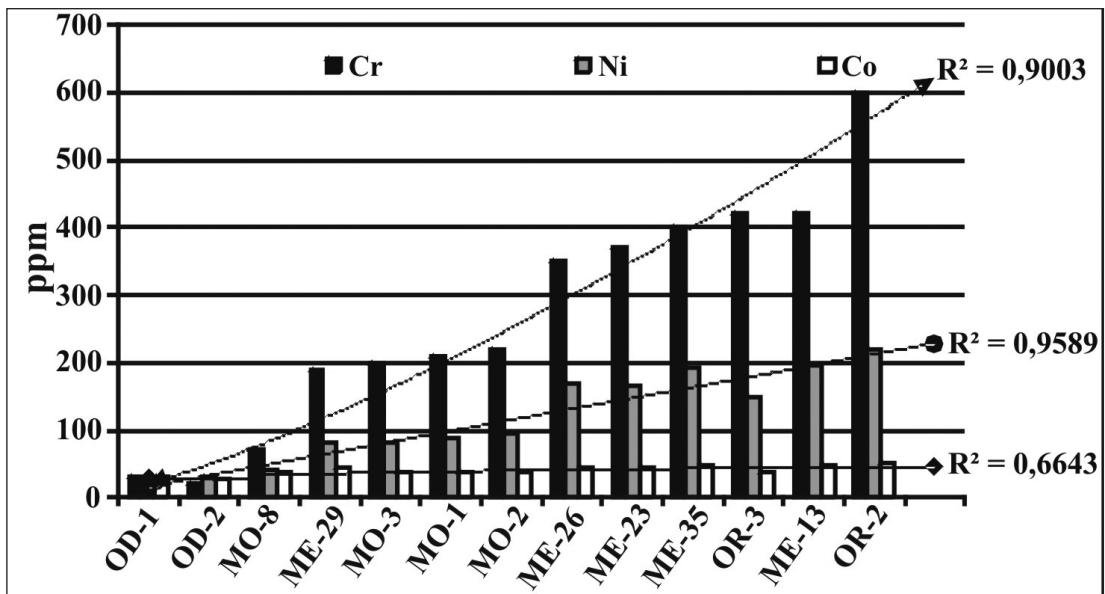


Figure 12- Columnar correlation diagram of Cr-Ni-Co elements ranging from fresh sample (OD-1) to rodingitized sample (OR-2). (See Figure 11 for sample sources).

Table 2- Gain (+) and loss (-) estimations of rodingites in terms of wt. % and ppm with respect to original rocks.

	Rodingite dyke of Van-Özalp Area							Tsiokuras et., al., 2000		Koutsovisit et., al., 2008	
	ME-26	ME-35	ME-13	ME-23	MO-1	MO-2	MO-3	OR-2	OR-3	OR-1	OR-4
SiO ₂	-5,85	-5,25	-10,15	-9,35	-10,45	-9,25	-6,55	-19,39	-20,04	-12,42	-15,02
Al ₂ O ₃	2,85	0,45	-2,05	-0,05	-1,10	-1,70	-1,55	-3,86	-1,94	-4,73	1,86
Fe ₂ O ₃	-3,21	-2,05	-2,29	-2,12	-2,35	-1,77	-1,60	0,84	-0,89	-0,91	1,30
CaO	4,15	3,65	8,40	9,30	13,90	12,30	9,50	8,98	13,70	13,79	10,64
MgO	2,20	2,97	2,87	2,34	0,03	0,27	0,04	11,19	7,65	8,09	3,39
Na ₂ O	-0,76	-0,69	-0,22	-1,43	-1,70	-1,58	-1,28	-1,73	-1,75	-5,22	-5,20
K ₂ O	-0,51	-0,40	-0,68	-0,67	-0,67	-0,65	-0,59	-0,11		-0,01	-0,05
TiO ₂	-0,25	-0,10	-0,13	-0,09	0,03	0,12	0,16	0,69	0,45	-0,03	0,20
MnO	-0,04	-0,02	-0,03	-0,02	-0,03	-0,02	-0,01	0,18	0,14	0,00	0,06
P ₂ O ₅	-0,02	0,00	-0,02	0,00	0,00	0,02	0,01	0,02	0,01	0,00	0,01
Co	1,95	5,95	5,05	3,15	-5,15	-2,95	-3,85	24,50	10,50		0,00
Cr	220,0	270,0	290,0	240,0	80,0	90,0	70,0	575,0	395,0	1444,0	228,0
Ni	108,0	131,0	135,0	104,0	29,0	33,0	20,0	195,0	125,0	412,0	37,0
Th	-0,21	-0,17	-0,20	-0,17	-0,13	-0,10	-0,06	-0,30	-0,32		-0,30
Ta	-0,10	-0,10	-0,10	0,00	0,00	0,00	0,00	-0,02			0,00
Nb	-1,15	-0,65	-0,75	-0,65	-0,15	0,15	0,35	-0,35	-0,45		1,00
Hf	-0,45	-0,15	-0,25	-0,15	0,05	0,15	0,35	0,90	0,60		0,70
Y	-7,30	-3,30	-4,30	-3,40	-1,50	0,10	1,60	15,55	11,35	2,50	5,20
Zr	-15,00	-4,00	-6,00	-4,00	2,00	8,00	11,00	20,50	14,50	-0,80	11,20
La	-0,65	-0,55	-0,85	-0,75	-0,35	0,05	0,25	-0,29	-0,42	-0,10	0,10
Ce	-1,65	-1,05	-1,65	-1,25	-0,35	0,55	1,25	0,55	0,07	-1,10	0,20
Pr	-0,29	-0,13	-0,20	-0,15	-0,03	0,09	0,19	0,36	0,26	-0,08	0,12
Nd	-1,25	-0,45	-1,05	-0,65	-0,05	0,45	1,05	3,17	2,48	-0,50	0,90
Sm	-0,48	-0,17	-0,23	-0,14	0,18	0,20	0,41	1,55	1,27	0,10	0,60
Eu	-0,17	-0,01	-0,07	-0,07	0,08	0,05	0,14	1,80	3,06	-0,05	0,11
Gd	-0,63	-0,19	-0,34	-0,27	-0,02	0,18	0,40	2,25	1,78	0,15	0,62
Tb	-0,15	-0,07	-0,10	-0,08	-0,02	0,00	0,05	0,47	0,35	0,06	0,15
Dy	-1,09	-0,47	-0,64	-0,46	-0,15	0,03	0,32	2,85	2,03	0,29	0,82
Ho	-0,28	-0,11	-0,16	-0,10	-0,05	0,01	0,05	0,54	0,39	0,09	0,20
Er	-0,85	-0,44	-0,58	-0,43	-0,16	-0,06	0,14	1,49	1,03	0,30	0,57
Tm	-0,14	-0,08	-0,09	-0,06	-0,06	-0,01	-0,01	0,20	0,13	0,08	0,10
Yb	-0,96	-0,49	-0,60	-0,54	-0,31	-0,16	-0,03	1,12	0,73	0,37	0,59
Lu	-0,14	-0,07	-0,10	-0,07	-0,06	-0,01	0,02	0,15	0,09	0,03	0,09

ues of MO-8 and ME-29 samples for the original rock in Van-Özalp field and average values of OD-1 and OD-2 samples and OMD-1 sample for Othrs were used in the table.

According to the results of Isocon method, it was seen that SiO₂, Na₂O, K₂O major oxides presenting negative (-) coefficient values were de-

pleted from original rocks in all rodingite samples. However; CaO and MgO major oxides presenting (+) coefficient values were enriched as a result of rodingitization. The assessment of samples which presents both (+) and (-) coefficient values in table 2 could be made by looking at the proportional difference between (+) and (-) coefficients. For example, Co as the transient element

has weighted positive coefficient values in rodingite samples with respect to the original rock. This situation indicates that Co element was enriched in rodingites. It can be stated that values most approaching to zero on the Table of Isocon analysis were relatively least affected from metasomatism. This especially comes out in values of trace and REEs of rodingites investigated. The ionic potential of five rodingite samples is approximately 7. However, it was observed that, Ta element, with its 0 (zero) ionic potential value, is the most immobile element during metasomatic processes among all elements. Zero integer is the immobility indicator in isocon analyses in which the mathematical proportionality was used. It is quite difficult although this value is expected to reach. Trace and REEs of rodingitized dykes in ophiolites in Van-Özalp field were enriched or depleted at various grades (though minimum) according to the results of isocon analysis. It is seen that this situation was mainly neutralized in terms of proportionality between the (+) and (-) coefficients in analysis results. Furthermore; coefficient values whether these are (+) or (-), are in less value ranges compared to Otrhys rodingites. Especially; Van-Özalp field rodingites of Ree, in samples MO-2 and MO-3, the depletion is observed in all Ree though less. However, all other Rees are enriched. Despite that, significant enrichments are generally observed in Ree contents of Otrhys rodingites with positive coefficient values. This is one of the most important differences between Otrhys rodingites and Van-Özalp rodingites. So; the metasomatic source which produced Otrhys rodingites must have been enriched by Rees more than the metasomatic source producing Van-Özalp rodingites. It is known that the alkalinity of fluids due to the intensity and result of equilibrium reactions have developed in metasomatic processes. The enrichment by Rees is normally expected as a result of reaction of alkaline fluids at high grades with peridotites forming the host rocks of dykes. This situation might have caused Ree enrichment in rodingite rocks at last stages of rodingitization.

Nevertheless; it is stated that peridotites of Otrhys ophiolite have been depleted by Lrees (Bizimis et al., 2000; Barth et al., 2003; Tsiokuras et al., 2009). Then, it can be considered that peridotitic pyroxenes have very little Lree addition to the metasomatic source.

RESULTS

Within the light of analytical data of mafic rocks which was investigated in this study, the equilibrium reactions of Ca metasomatism despite the enrichment in CaO values in these rocks were encountered by the depletion in SiO_2 values. As a result of reaction of Ca-Mg silicates with calcic plagioclases, the grossularite (hydrogrossularite) and chlorite which are the characteristic minerals of rodingites are formed as the secondary products. Therefore; a distinct increase in MgO values in rodingites was encountered. However; there was not observed a significant change in Al_2O_3 and Fe_2O_{3t} values. Whereas; transients metals such as; Cr, Ni, Co are enriched in rodingites.

Geochemical analysis values of diabase dyke samples taken from Özalp ophiolites and dolerites and rodingites samples belonging to Otrhys ophiolite were correlated. This correlation indicated that, differences in rock chemistry found at the source area where Ca metasomatism had occurred could cause significant changes over the element mobility during rodingitization process.

Th, Ta, Nb, Hf, Ti and REEs are used as reliable indicators in petrogenetic interpretations of ophiolitic mafic rocks. It was determined that these elements were not relatively affected from Ca metasomatism at rodingitization grades which could both petrographically and geochemically be distinguished in mafic rocks of Özalp region. In addition to other trace elements except for Ta element, there is a relative mobility in Otrhys dolerites due to rodingitization in REEs as well. There was not observed a distinct mobility

in contents of trace and REEs mentioned in rodingitized dykes of the study area. Despite that, the overall element enrichment in rodingitized dykes of Otrhys was encountered. However, it is considered that the metasomatic source which produced Otrhys rodingites might have been enriched by fluids that had interacted with more enriched rocks in terms of element contents due to local geological factors in the region. Besides; these changes also depend on the regional geology, tectonical setting of the environment, the factors such as temperature, oxygen fugacity and chemical composition of fluids that might have developed and on the rodingite development that had occurred at various stages.

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