

Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 99	263-270	Thessaloniki 2010
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THE GEOCHEMISTRY AND PETROGENESIS OF VOLCANIC ROCKS WITHIN OPHIOLITIC FORMATIONS AT THE NORTHEAST OTHRIS REGION, GREECE

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Abstract: Volcanic rocks from ophiolitic formations in northeast Othris region are categorized based on their geochemical characteristics in two distinct groups. The first includes volcanic rocks from the ophiolitic formations of Eretria and Velestino, which, as their immobile element chemistry and geochemical plots indicate, seem to have formed in an N-MORB environment with 5-15% partial melting of a fertile or moderately depleted mantle source and extensive fractional crystallization processes. The second group is exclusively from the ophiolitic formation of Aerino having rocks with generally higher MgO contents, subduction related features (e.g. low Ti/V<10) and having been derived from a highly depleted mantle source but with similar partial melting degrees (10-20%). These differences may reflect an evolution from an earlier MORB to a latter IAT volcanism within the same oceanic basin or correspond to two separate oceanic environments.

Keywords: Othris, Ophiolites, Volcanism, N-MORB, IAT.

1. Introduction

The formation and emplacement of ophiolites in Central Greece has been an area of extensive research and discussion for many years. The Othris region is of great importance in understanding the evolution of the Greek ophiolites but also the geotectonic environment in the key area of Central Greece during Mesozoic times. The main ophiolitic complex of Othris, which has been comprehensively studied (e.g. Ferrière, 1982; Jones & Robertson, 1991; Spray et al., 1984; Smith & Rassios, 2003; Tsikouras et al., 2009), lies in the western part of the region and has been dated as Jurassic. In the northeastern part of Othris and specifically in the areas of Eretria, Velestino and Aerino ophiolitic rocks occur (Fig. 1), consisting mainly of serpentinized ultrabasic rocks, few gabbroic and rare doleritic dykes and basaltic pillow lavas, usually metamorphosed and/or metasomatized and schistosed. It is unclear if these ophiolitic rocks are dismembered parts of the Othris ophiolite or they have been generated in the Vardar Ocean and later on overthrust in their present site. In this paper we focus on the geochemistry and petrology of the Eretria, Velestino and Aerino volcanics (s.l.),

which may provide evidence for the petrogenesis and geotectonic origin of the related ophiolites.

2. Geological setting

The Eretria ophiolitic formation has been studied by Ferrière (1982), Economou & Naldrett (1984) and Migiros et al. (1997). The later authors, who do not to preclude a Cretaceous age for this formation, divided the Alpine rocks of the Eretria region in three stratigraphic units: The lowest unit is a tectonic mélange which includes sedimentary rocks, cipolin marbles and mostly highly altered metabasic rocks (Asprougia unit). The intermediate unit consists of metaclastic and metabasic rocks (Paliambela unit), while the upper unit represents serpentinized ultrabasic rocks (Eretria unit). The ophiolites are locally covered by sedimentary rocks of the Eastern Greece unit (Papanikolaou, 2009). These rocks were formed during the period between Upper Cretaceous and Eocene mostly consisting of crystalline limestones locally dolomitic, medium to thickly layered and at the upper parts flysch which consists of red shales and phylites alternating with thin bedded limestones, sandstones and conglomerates (Smith et al., 1975; Mi-

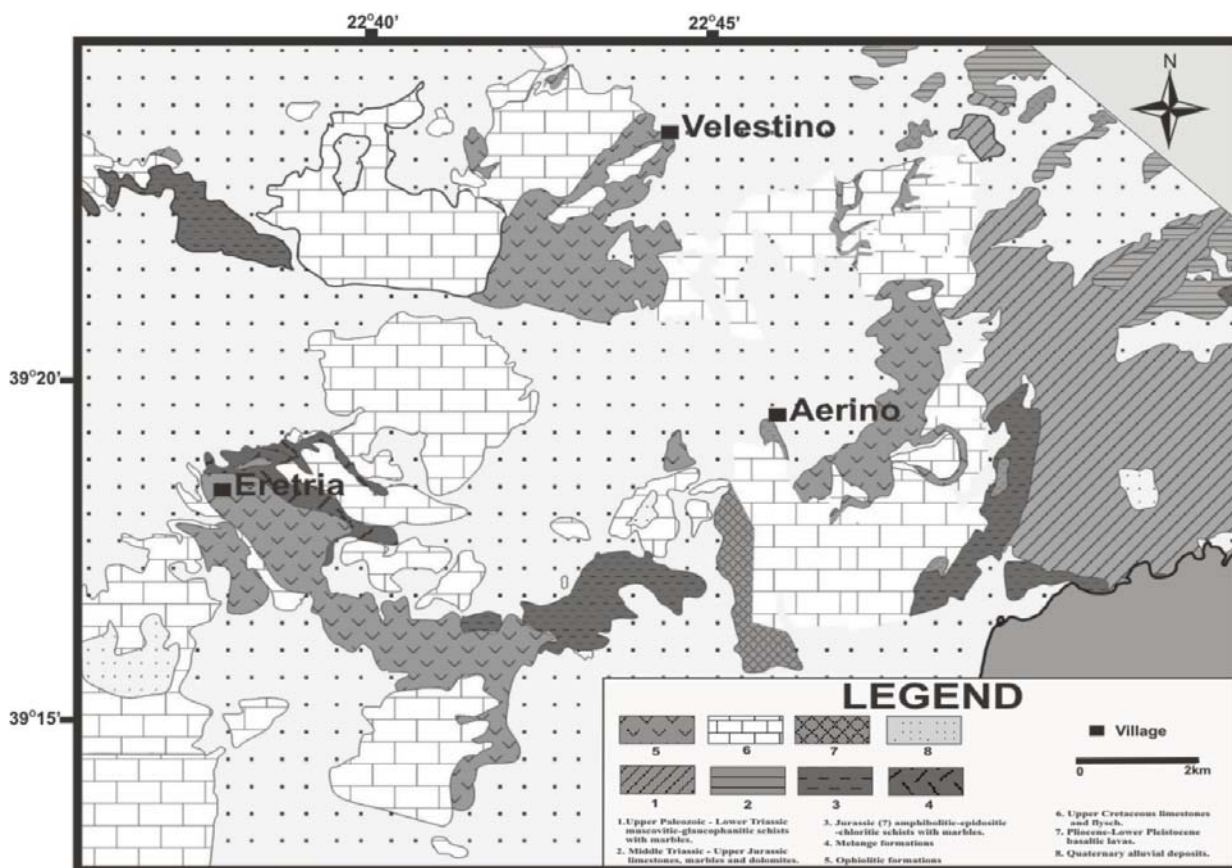


Fig. 1. Geological map of the south region of Othris.

giros, 1990; Katsikatsos, 1992; Papanikolaou, 2009). It is not clear from the existing literature whether the Eretria ophiolite and associated mélangé rocks belong to the uppermost unit of Maliac Zone or they belong to the pre-Cretaceous ophiolitic nappe of the Pelagonian Zone supposed to be originated from overthrust Maliac Zone rocks onto the Pelagonian continental margin. The ophiolitic formations of Aerino and Velestino are interpreted as being parts of the post-flysch tectonic nappe which is overthrust above the carbonates and flysch of the Eastern-Greece unit and rooted in the Mesozoic Vardar Ocean (Katsikatsos, 1992; Pe-Piper & Piper, 2002). The later nappe composes medium-layered crystalline limestone and an ophiolitic complex consisting mainly of serpentinites and a remarkable network of dykes, which are pyroxenites, gabbros and dolerites frequently rondigitized. Greenschists and thin layers of cipolin marbles and radiolarites occur in the deeper parts of Aerino and Velestino ophiolitic rocks.

3. Analytical techniques

Whole rock chemistry analyses were performed at

ACME Analytical Laboratories LTD, Vancouver, Canada. Major elements were determined by ICP-ES method, trace elements and REE obtained by ICP-MS method and through XRF analyses. Total carbon and sulfur concentrations were simultaneously determined using a LECO® induction furnace.

4. Petrography and bulk-rock chemistry

All studied rocks have undergone post-magmatic alteration processes, so sampling was carefully carried out as to collect the least altered samples. The collected samples were petrographically studied, while six representative samples were chemically analyzed for major and trace elements (Tab. 1). Five are from doleritic dykes in Aerino and Velestino and one is from a small occurrence of pillow lava in Eretria possibly belonging to the Paliambella unit.

From a geochemical point of view two groups of samples were distinguished: "Group I" includes samples with very high Σ REE contents, which are the ones from Eretria and Velestino, while "Group II" includes the samples from Aerino which have much lower Σ REE contents (Tab. 1). Based on Total Alkali - Silica (TAS) classification scheme

Table 1. Whole-rock major element (wt %) and trace element (ppm) compositions of samples studied, measured by XRF and ICP-MS, with classification and location information. Major elements, Ni, Cr, V, Cu and Zn were by measured by XRF. Others were measured by ICP-MS. Total iron given as FeO*. LOI: Loss On Egnition. b.d.l.: below detection limit.

Sample:	EX11/AER	263/AER	272/AER	266/AER	251/VEL	281/ERE
Rock type	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Pillow lava
TAS classification	High-Mg Boninite	Boninite	Boninite	Basaltic andesite	Basaltic andesite	Basaltic andesite
Location	Aerino	Aerino	Aerino	Aerino	Velestino	Eretria
latitude (^o N)	39°19'49"	39°19'94"	39°19'39"	39°19'98"	39°22'40"	N39°18'12"
longitude (^o E)	22°47'68"	22°48'00"	22°47'61"	22°47'788"	E22°43'25"	E22°37'92"
SiO ₂	49,13	53,88	52,06	53,02	53,15	55,45
TiO ₂	0,29	0,26	0,35	0,31	1,15	2,36
Al ₂ O ₃	11,70	15,42	12,76	15,74	14,78	11,56
FeO*	9,39	8,31	8,18	6,87	9,24	10,16
MnO	0,18	0,16	0,18	0,10	0,13	0,18
MgO	13,06	8,14	10,78	6,87	6,55	6,54
CaO	8,56	5,74	9,35	9,74	7,67	7,63
Na ₂ O	1,79	5,24	3,34	4,66	4,07	4,84
K ₂ O	0,04	0,05	b.d.l.	b.d.l.	0,92	0,11
P ₂ O ₅	b.d.l.	0,02	0,03	0,02	0,14	0,23
LOI	5,60	2,80	3,00	2,70	2,90	1,50
Total	99,75	100,03	100,04	100,03	100,72	100,56
Sc	51	42	44	41	40	36
V	271	259	255	274	218	357
Cr	858	84	550	106	148	42
Co	56	37	42	39	38	44
Ni	93	47	109	48	69	30
Cu	2	13	2	5	3	11
Zn	28	22	20	7	21	11
Rb	0,6	b.d.l.	b.d.l.	b.d.l.	16,6	0,6
Sr	13,3	157,2	12,2	60,4	110,4	81,6
Y	6,6	5,8	8,9	7,9	34,9	50,3
Zr	21	6,9	10,4	8,9	98,2	148,7
Nb	1	b.d.l.	b.d.l.	b.d.l.	2,3	3,8
Cs	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0,3	b.d.l.
Ba	3	4,5	0,9	13,9	36,3	25,3
Hf	0,7	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4,4
Ta	0,1	0,1	0,1	0,2	0,2	0,4
Pb	0,1	0,2	0,2	0,3	0,1	0,4
Th	b.d.l.	0,3	0,1	0,1	0,2	0,4
U	0,1	0,2	0,1	0,1	0,1	0,1
La	0,80	0,70	0,90	0,60	4,30	6,30
Ce	1,70	1,80	2,30	1,80	12,80	19,10
Pr	0,25	0,20	0,32	0,24	2,06	2,89
Nd	1,00	1,10	1,70	1,10	10,50	15,10
Sm	0,4	0,2	0,8	0,6	3,6	5,2
Eu	0,22	0,15	0,24	0,19	1,40	1,67
Gd	0,64	0,60	1,12	0,84	5,05	6,74
Tb	0,15	0,12	0,22	0,19	0,93	1,36
Dy	0,97	0,92	1,40	1,36	5,91	8,47
Ho	0,24	0,19	0,32	0,29	1,24	1,81
Er	0,75	0,64	0,98	0,88	3,68	5,71
Tm	0,12	0,09	0,16	0,14	0,61	0,85
Yb	0,80	0,77	0,99	0,92	3,58	5,49
Lu	0,13	0,13	0,16	0,15	0,57	0,82
TOT/C	b.d.l.	0,01	0,01	0,01	0,11	0,02
TOT/S	b.d.l.	b.d.l.	0,01	b.d.l.	0,01	0,01
ΣREE	8,17	7,61	11,61	9,30	56,23	81,51

“Group II” rocks are basaltic andesites (Fig. 2). Their mineral constituents vary from fine to medium grained and consist mainly of plagioclases, clinopyroxenes, secondary amphiboles and minor devitrified glass. Clinopyroxenes are subhedral and marginally altered. Plagioclases are also subhedral and form with the clinopyroxenes mainly subophitic textures. Accessory minerals include spinel, magnetite and ilmenite. Secondary minerals include epidote, pumpellyite, chlorite, quartz, calcite and titanite. The subophitic textures appear between clinopyroxenes and plagioclases, while hyalophitic between plagioclases and glass (devitrified). Small amygdales of calcite and chlorite appear in spherical form and in some cases are zoned.

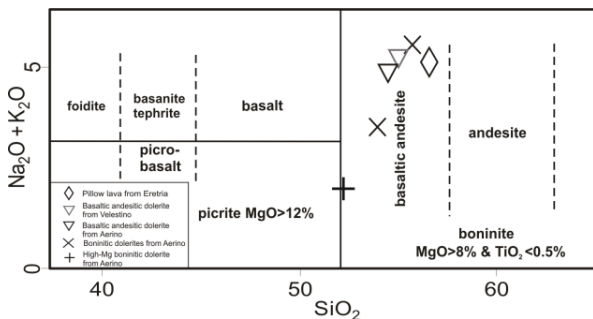


Fig. 2. Classification binary diagram of Na₂O+K₂O against SiO₂ with the fields drawn according to Le Bas et al. (2000).

“Group II” rocks are dolerites of boninitic and basaltic andesitic composition (Tab. 1, Fig. 2). The boninitic rock with the highest MgO content (13.06 wt%) (named thereafter high-Mg boninite) consists mainly of clinopyroxenes, secondary amphiboles, plagioclases and chlorite after devitrified glass. Accessory minerals include spinel and magnetite. Serpentine appears in the form of small scattered crystals, possibly replacing olivine or orthopyroxenes. The rock is mostly microcrystalline with orientation, except for some medium grained clinopyroxenes which are altered at their rims. The boninitic dolerites (called thereafter boninites) consist of secondary amphiboles, clinopyroxenes, plagioclases, and devitrified glass mostly of chlorite. The presence of minerals such as pumpellyite, epidote, chlorite and prehnite verify that the rocks underwent low grade oceanic metamorphism. Calcite and chlorite also appear in the form of amygdals. Accessory minerals include spinel, magnetite, titanite and quartz. The matrix presents mainly subophitic textures, while between plagioclases and amphiboles textures are poikilitic. The basaltic andesitic dolerite has the same primary and sec-

ondary mineral phases as boninites, with abundant plagioclases and with absence of orientation. Textures are similar and the accessory minerals include titanite, ilmenite, spinel, magnetite, calcite, zircon and apatite.

High-Mg rocks appear only in Aerino. All rocks are subalkaline due to their relatively low Na₂O + K₂O contents (1.9-5.4 wt%), and are tholeiitic as seen in the binary diagram of figure 3. None of the studied rocks can be characterized as Fe-Ti-rich since the ratio FeO_t/MgO presents values lower than 1.75 (Melson et al. 1976; Sinton et al. 1983).

“Group I” rocks have subparallel REE patterns (Fig. 4). The LREE values are high ranging between 18.1-33.0 X CN, with small increase in their MREE values (24.0-35.1 X CN) and similar HREE values (22.2-35.7 X CN). The (La/Sm)_{CN} and (La/Yb)_{CN} values range between 0.75-0.76 and 0.78-0.82 respectively. “Group II” rocks present

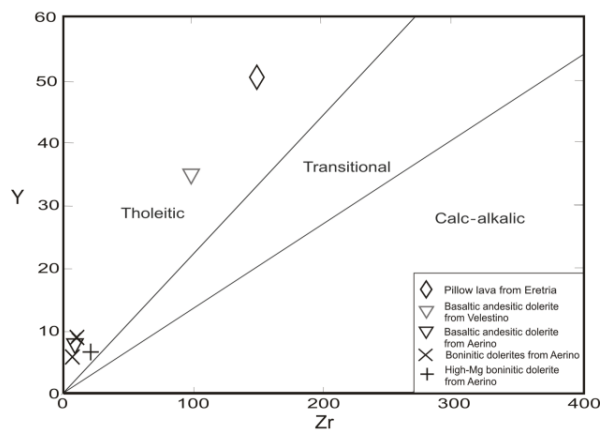


Fig. 3. Binary diagram of Y against Zr (Barrett & Maclean, 1999).

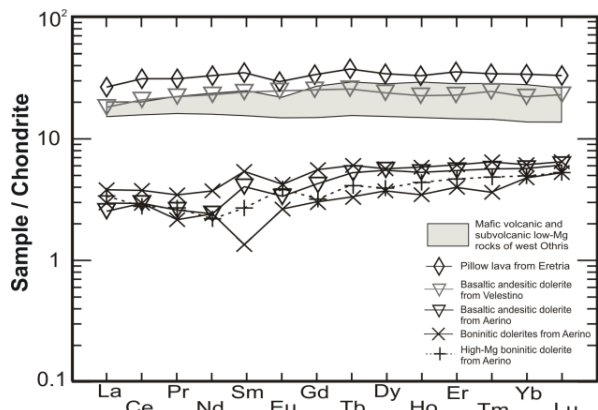


Fig. 4. Chondrite-normalized REE patterns [normalization factors from McDonough & Sun (1995)] of the volcanic rocks from the ophiolitic occurrences in northeast Othris. Grey field shows the REE patterns of mafic volcanic rocks from west Othris (Bortolotti et al., 2008).

subparallel REE patterns (Fig. 4) with the LREE values ranging between 2.2-3.8 X CN, broader ranging MREE values (1.4-5.7 X CN) and higher HREE values (2.2-6.5 X CN). The $(La/Sm)_{CN}$ and $(La/Yb)_{CN}$ values range between 0.62-2.19 and 0.44-0.68 respectively. In the primitive mantle normalized multi-element diagram (Fig. 5) it has been noticed that K, Sr, U and Pb vary a lot and will be considered with due cause as the original magmatic values, since alteration affected the studied rocks and these elements are highly mobile. ‘Group I’ rocks present similar patterns with high HFSE normalized values ($Yb_{PN}=8.1-12.4$ X PM), noticeable negative Pb anomalies and small or no negative Ti anomalies. ‘Group II’ rocks have lower HFSE normalized values ($Yb_{PN}=1.81-2.24$ X PM.). The high-Mg boninite presents a significant positive Zr anomaly, while the boninites and the basaltic andesitic dolerite present small or no negative Zr anomalies. All these samples have significant positive Pb anomalies and noticeable higher U primitive mantle normalized values compared to Nb and Ta.

5. Discussion

Each one of the two groups of rocks seems to have been created in a different geotectonic environment. The discrimination diagram of figure 6, as well as other discrimination diagrams (not shown), indicate that ‘Group I’ rocks were formed in MORB or BAB environment, while ‘Group II’ in an IAT environment. The multi-element patterns of ‘Group I’ rocks are subparallel to both low-Mg N-

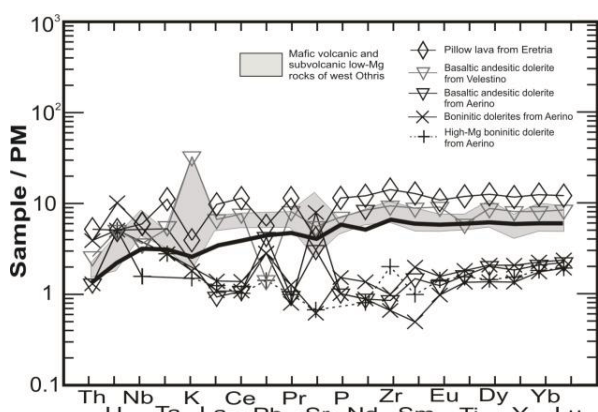


Fig. 5. Primitive mantle-normalized multi-element patterns [normalization factors from McDonough & Sun (1995)] of the volcanic rocks from the ophiolitic occurrences in northeast Othris. Grey field shows the REE patterns of mafic volcanic rocks from west Othris (Bortolotti et al. 2008). Thick dark line represents the ideal N-MORB element composition from Sun & McDonough (1989).

MORB volcanic rocks present in the Jurassic ophiolitic sequence (Fourka Unit) of west Othris (Bortolotti et al., 2008) and to the ideal N-MORB pattern (Sun & McDonough, 1989), especially concerning the HFSE (Fig. 5). The significant positive Pb anomalies may be partly due to subduction related processes but alteration should have changed the original magmatic values. U primitive mantle normalized values are higher compared to the normalized Nb and Ta values which may be attributed to subduction processes (Pearce & Peate, 1995). The pillow lava sample 281/ERE has a negative anomaly ($Eu_{CN}/Eu^*=0.86$) which may be attributed to plagioclase fractionation or change in the fO_2 conditions (Drake & Weill, 1975). Eu anomalies are positive for the high-Mg boninite (sample EX11/AER) and the boninite sample 263/AER, and negative for samples 272/AER and 266/AER. This can be seen in the range of the ratio Eu_{CN}/Eu^* (0.77-1.32) which may probably be attributed to changes in fO_2 conditions rather than plagioclase fractionation processes. This is interpreted by the complete absence of any correlation between the Eu_{CN}/Eu^* ratio and either SiO_2 , Cr or Ni. However metasomatic process may have also affected Eu values.

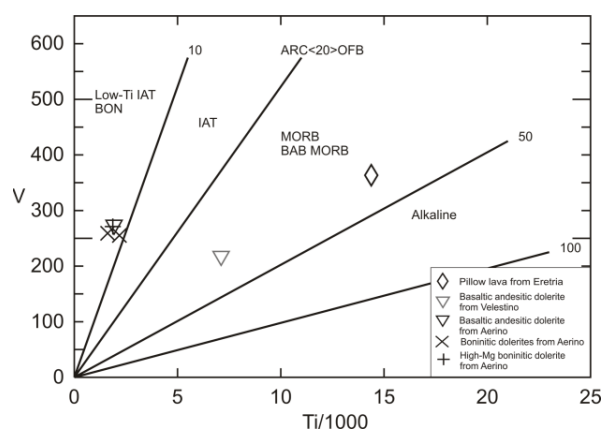


Fig. 6. Discrimination diagram of V vs. Ti/1000 (Shervais, 1982). MORB=mid-ocean ridge basalts, IAT=Island arc tholeiites, Bon=boninites.

Positive and negative Zr and Sm anomalies in the ‘Group II’ rocks (Fig. 5) may indicate that there was a change in the mantle source mineralogy or that the melting degrees changed. Whatever is the case, these rocks did not form simply from fractionation processes of a primary melt as indicated by the fact that ΣREE values do not always increase with increase of MgO. Zr/Sm ratio values are considered by researchers (e.g. Wolde et al., 1996) as an indicator for clinopyroxene proportion in the

mantle source. Samples EX11/AER and 263/AER have high Zr/Sm (39-56) and low Sm/Yb values (0.26-0.5), while samples 272/AER and 266/AER have low Zr/Sm (13-28.6) and high Sm/Yb values (0.65-1). This shows that the first set of rocks are closer related to a highly depleted mantle source while the second with a moderately depleted mantle source. In order to better estimate the composition of the mantle source and the degrees of partial melting, the studied rocks were examined according to their concentrations of highly incompatible to compatible elements. These are Nb and Zr (very highly incompatible, VHI), Ti, Y and Yb (highly incompatible, HI), Ca, Al, V and Sc (moderately incompatible, MI), Mn and Fe (slightly compatible), Co and Mg (moderately compatible, MC), and Cr and Ni (highly compatible, HC). Comparisons are made in the normalized multi-element diagram of figure 7 against a FMM (Fertile MORB Mantle), according to Pearce & Parkinson (1993). "Group I" rocks show VHI>HI>MI patterns, which correspond to relatively low or medium partial melting degrees of a fertile mantle source. Excluding the high-Mg boninite "Group II" rocks show VHI<HI<MI patterns, which are accounted for rocks that formed from relatively high degrees of a depleted mantle source. The high-Mg boninite has VHI>HI<MI pattern which shows that it formed similarly with the rest of the rocks of "Group II" but with re-enrichment of the VHI elements.

The above observations seem to fit well when projecting the studied rocks in the petrogenetic diagram of figure 8. Primary magma for the rocks from "Group I" seems to have been formed either with 10-15% partial melting of a fertile mantle

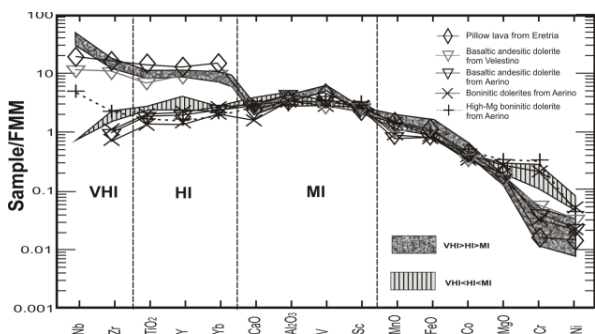


Fig. 7. FMM (fertile MORB mantle)-normalized patterns for the volcanic rocks from the ophiolitic occurrences in northeast Othris. Normalizing values are from Pearce & Parkinson (1993), are: Nb (0.2), Zr (9.2), TiO₂ (0.175), Y (3.9), CaO (3.25), Al₂O₃ (3.75), V (78), Sc (15.5), MnO 0.13), FeO (8.8), Co (106), MgO (38.4), Cr (2500), Ni (2020). Oxides in wt.%, elements in ppm.

source (FMM or PM) (Bédard 1999; McDonough & Sun 1995) or with 5-10% partial melting of a moderately depleted mantle source (DMM) (Workman & Hart 2005). Fractional crystallization seems to have played a significant role as indicated by their low Cr contents. Additionally N-MORB metabasalts and metadolerites from Eretria (Migirios et al. 1997) are also plotted in Figure 8 showing similar petrogenetic evolution processes. The primary magma for the rocks from "Group II" appears to have formed with 10-15% partial melting of a highly depleted mantle source (M3) (Murton 1989), rather than very high degrees of the DMM mantle source (over 40%) which seems unrealistic. Fractional crystallization processes probably played an important role for samples 263/AER and 266/AER (low Cr contents). In the petrogenetic binary diagram of figure 9 all samples plot within the field defined by the melting curves from plagioclase or spinel peridotite mantle sources, whether enriched or depleted. This shows melting occurred in an upper mantle source where garnet was not present. Taking under consideration the referred fractional crystallization processes "Group I" rocks could have been produced from either the FMM or

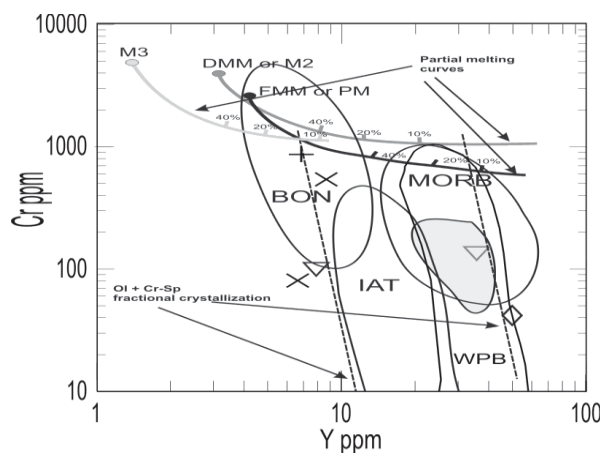


Fig. 8. Petrogenetic binary diagram of Cr vs. Y for the volcanic rocks from the ophiolitic occurrences in northeast Othris. DMM (or M2) and M3 mantle source compositions are from Pearce (1982), Murton (1989) and Workman & Hart (2005), while FMM (Fertile MORB Mantle) and PM mantle source compositions are from Bédard (1999) and McDonough & Sun (1995). The melting curves are designed for mantle source with mineral proportion ol0.60px0.2cpx0.1pl0.1, and melt mode proportion 3:1:4:4, while fractional crystallization lines were drawn for ol90Cr-sp10 (Pearce, 1982). The designed fields of MORB, IAT, WPB and Bon (boninites) are from Pearce (2003) and Dilek et al. (2007). Legend as seen in fig. 7. Gray field correspond to metabasaltic and metadoleritic rocks from Eretria (Migirios et al., 1997).

DMM mantle sources with the referred partial melting degrees. The relatively undifferentiated samples EX11/AER and 272/AER from “Group II” seem also to agree with the referred partial melting degrees (10-15%).

Taking under consideration the above described differences on geochemical data and petrogenetical history for the two Groups, and the fact that “Group I” presents similarities with west Othris Jurassic ophiolite, lead us to the assumption that the volcanic rocks of the ophiolitic occurrences in northeast Othris may belong either to two different Mesozoic ophiolitic sequences e.g. Vardar and

extraction and affected by a subduction episode. On the other hand, the present geochemical data and petrologic analysis reveal that the hypothesis Aerino and Velestino volcanic rocks would have parallel origin and emplacement history, as being parts to the same post-flyschic tectonic nappe and they are not very far from each other, seem not to be realistic at least regarding to their petrogenetical evolution. In contrast, Velestino and Eretria extrusive ophiolitic rocks are compositionally similar to volcanics from the Othris ophiolitic complex mainly developed few tens km south-westward of them.

6. Conclusions

The studied volcanic/subvolcanic rocks of the ophiolitic complexes in northeast Othris were found as dykes in Aerino and Velestino areas and as pillow lavas in Eretria. They can be classified in two groups: the high Σ REE basaltic andesites from Velestino and Eretria belong to the “Group I” rocks, whereas the low Σ REE dolerites from Aerino, which compositionally are boninites and basaltic andesites consist the “Group II”. “Group I” rocks resemble N-MORB basalts and seem to have been formed with 5-15% partial melting of a fertile or moderately depleted mantle source, followed by extensive fractional crystallization processes. They are very similar to the volcanic rocks present in the ophiolitic sequence of west Othris (Bortolotti et al. 2008). “Group II” rocks seem to have been generated by 10-20% partial melting of a highly depleted mantle source in a subduction environment, with some samples having been affected by fractional crystallization processes. From a geotectonic point of view the geochemical and petrogenetic diversities between the two Groups may either reflect a change from an earlier MORB to a latter IAT setting within the same oceanic basin during M. Jurassic – L. Cretaceous or correspond to volcanism taken place in two separate oceanic environments within the same time span.

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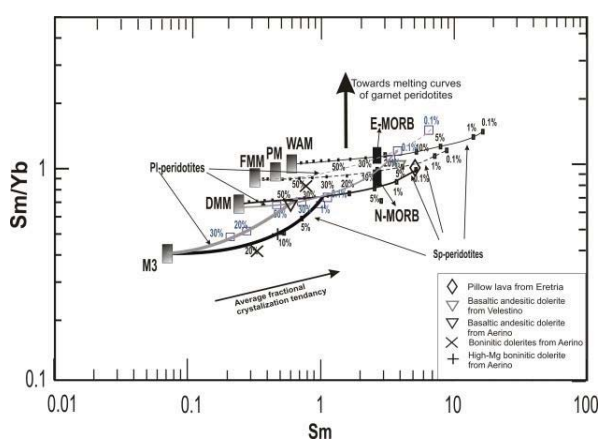


Fig. 9. Petrogenetic binary diagram of Sm/Yb vs. Sm in logarithmic scale for the volcanic rocks from the ophiolitic occurrences in northeast Othris. Melting curves have been designed using the non-modal batch partial melting equation of Shaw (1970). Melting curves were designed for spinel lherzolite with mineral proportions of $ol0.530 + opx0.270 + cpx0.170 + sp0.030$ and melt mode proportions $ol0.060 + opx0.280 + cpx0.670 + sp0.110$ (Kinzler, 1997). Partition coefficients are from McKenzie & O’Nions (1991, 1995) and normalizing values are from McDonough & Sun (1995). N-MORB and E-MORB compositions from Sun & McDonough (1989). Mantle sources are WAM (Aldanmaz et al., 2000), PM (McDonough & Sun, 1995), FMM (Bédard, 1999), DMM (Workman & Hart, 2005), while M3 is produced from 12% MORB extraction of DMM.

Othris ophiolitic complexes, with the later complex generated in the Pindos Ocean, or belong to a single basin, which in this case the basin is where Jurassic Othris ophiolite generated. For establishing the two basins model much more data from nearby regions is needed. If we assume the single basin model, the “Group I” rocks may resemble volcanic activity in a mid ocean ridge setting, while “Group II” rocks are the products of a later stage volcanism, with the mantle source depleted due to MORB

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