# Calc-alkaline volcanic rocks in mélange formations from the South Othris region, Greece: Petrogenetic and geotectonic implications

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**Abstract.** Volcanic rocks present in Mid-Mesozoic ophiolitic mélange formations at the South Othris region show calc-alkaline affinities and a broad compositional range from basic to felsic. Mineralogical and geochemical features are interpreted as having been strongly influenced by subduction related processes. Volcanics with similar major and minor element contents as well as geochemical characters have been reported in other regions in Central Greece and have been attributed to volcanism which occurred between the Middle and Upper Triassic. In the Othris region the confirmed Triassic volcanism is expressed by rift-related alkaline and E-MORB transitional rocks with OIB and MORB affinities, which however present *REE* similarities with the studied rocks. Petrogenetic modeling shows that the calc-alkaline volcanism could have been formed by addition of subduction fluids in the system that produced E-MORB volcanism and possibly at relatively high fractional crystallization degrees. This may reflect a change in the early rifting environment which occurred after the breakup of the Gondwana continental margin.

Key words: Othris, mélange formations, calc-alkaline lavas, Triassic oceanic basin.

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### Петрос Куцовитис, Андреас Маганас, Атанасиос Катеринопулос. Калциевоалкални скали в меланжа от района Южен Отрис, Гърция: Петрогенетични и геотектонски изводи

Резюме. Вулканските скали, разкриващи се всред средномезозойските офиолитови меланж формации от района Южен Отрис имат калциевоалкален характер и широк размах на състава – от базични до кисели. Минераложките и геохимични им особености са интерпретирани като силно повлияни от свързани със субдукция процеси. Вулканити с подобно съдържание на петрогенни оксиди и елементиследи, както и на геохимичния им характер са известни в други райони на Централна Гърция и са отнесени към вулканизма, проявен между средния и късен триас. В района Отрис триаският вулканизъм е алкален рифтов и преходноалкален Е-MORB с ОІВ и МОRВ характеристика, който обаче има подобни съдържания на *REE* като разглежданите вулканити. Петрогенетичното моделиране показва, че калциевоалкалният вулканизъм вероятно е формиран с привнос на субдукционни флуиди от магмена система, която е дала Е-MORB вулканизъм с възможна относително висока степен на фракционна кристализация. Това вероятно показва някаква смяна в ранната рифтова обстановка, която се проявява след разкъсването на Гондванския континентален ръб.

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# Introduction

The Othris region is known mostly for its ophiolites, occurring mainly in the western area and has been studied by many researchers (e.g. Smith et al. 1975; Price 1977; Ferrière 1982; Spray et al. 1984; Jones & Robertson 1991; Smith & Rassios 2003). However, a large part of the region is not only covered by ophiolites, but also by a widespread Triassic sequence of volcanic and sedimentary rocks (e.g. Roddick et al. 1979; Ferrière 1982; Smith & Rassios 2003) and also of smaller occurrences of mélange formations (Nisbet 1974; Ferrière 1982). The evolution of the oceanic basin which gave birth to the magmatic rocks of Othris has been a field of productive dispute for over the last 30 vears. Many questions lie not only about the geotectonic environment and the petrogenetic processes which took place, but also on the number of oceanic basins which contributed to the formation of Othris magmatic rocks. Unanswered questions may be attributed to many factors such as alteration, intense and multistage tectonic processes and also to the fact that more than half of the region is covered by either a thick Upper Cretaceous sedimentary sequence or Quaternary alluvial deposits.

In this paper we focus on volcanic rocks from two Mid-Mesozoic ophiolitic mélange formations in the southeastern region of Othris, which are tectonically emplaced on top of the volcanic and sedimentary Triassic sequence. We examine whether these rocks are more related to the Triassic volcanism or to the Jurassic ophiolitic rocks of the region, and which petrogenetic processes led to the formation of these rocks. Petrological interpretations of these rocks could shed light on the evolution stages of the oceanic basin and may elucidate a case of a subduction episode that took place in an otherwise rift related environment.

## **Geological setting**

The region of Othris consists of 3 main geological zones, the Pelagonian (Ferriere,

1982; Smith & Rassios 2003), the Sub-Pelagonian or Maliac (Smith et al. 1975; Smith 1979; Ferrière 1982; Smith & Rassios 2003) and the Eastern-Greek zone (Papanikolaou 1997). The Sub-Pelagonian zone includes a Lower to Middle Triassic (Werfenian to Anisian) sedimentary sequence consisting of limestones which at the bottom are dolomitic or marly, whereas at the upper parts are siliceous or brecciated. They have been dated based on their fossils which are ammonites, lamellibranches, poorly preserved gastropods, and foraminifera (Smith et al. 1975; Ferrière 1982). According to Price (1977) these are connected to the rifting stage which took place in the Triassic period. These rocks are overlaid by a volcanic and sedimentary sequence which covers a large part of Othris, mostly in the central region (Smith & Rassios 2003). The volcanic rocks consist mainly of transitional and rarely alkaline pillow lavas (Tsikouras et al. 2008; Monjoie et al. 2008). In the central parts of the Othris region (Fig.1) a series of Upper Triassic to Middle Jurassic siliceous and dolomitic limestones appears (Smith et al. 1975; Ferriere 1982). The Sub-Pelagonian zone also includes mélange formations, e.g. these in Paleokerasia and Agios Georgios, which are tectonically emplaced over the Triassic volcanic and sedimentary rock sequence. The tectonic emplacement of the Paleokerasia mélange is confirmed by the presence of gneisses in the western part, separating it from the Triassic sequence. Most of the rocks of the Paleokerasia mélange are volcanic and sedimentary rocks, with the first being represented by highly altered pillow lavas, but also by minor occurrences of felsic rocks. The Agios Georgios mélange formation also consists of highly altered pillow lavas, as well as serpentinites and sedimentary rocks such as sandstones and radiolarites.

The Eastern-Greek zone includes rocks formed during the period between Late Cretaceous and Eocene, when transgression of the sea covered earlier rocks, belonging to the Maliac (or Subpelagonian) and Pelagonian



Fig. 1. Simplified geological map of the southern region of Othris

zones (Papanikolaou 1997, 2009). The lower formation of the Eastern-Greek zone can be considered as clastic one, consisting of sandstones, shales, conglomerates and intercalations of sandy and marly limestones, dated Aptian-Albian to Upper Turonian-Coniacian (Smith et al. 1975; Katsikatsos 1986; Papanikolaou 1997, 2009). The most frequently occurring formation is the intermediate, which contains Upper Cretaceous carbonaceous rocks. Specifically the rocks are crystalline limestones, locally dolomitic, with microfauna, assigning age between Cenomanian and Campanian. They appear medium to thickly bedded and evolve in the upper parts to clastic and brecciated imbricated limestones (Smith et al. 1975; Ferriere 1982; Katsikatsos et al. 1986). The upper formation includes Paleocene to Lower Eocene flysch, consisting of red shales and phyllites which alternate with thin bedded limestones, sandstones and conglomerates and in some cases with ophiolitic olistholiths (Katsikatsos et al. 1986).

### **Analytical procedures**

Mineral chemistry analyses were performed at the Department of Lithospheric Research, University of Vienna and at the University of Athens, Department of Mineralogy and Petrology Laboratory. At the University of Vienna we used a CAMECA SX-100 electron probe Xray microanalyser equipped with 4 wavelengthdispersive and 1 energy-dispersive spectrometers. Operating conditions were: accelerating voltage of 15 kV, beam current 20 nA. The beam size was 1 µm for all minerals. At the University of Athens analyses were obtained using a scanning electron microscope (SEM) JEOL-5600 (EDS).

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, while C and S by LECO instruments.

### Results

### Bulk-rock chemistry

The pillow lava rocks from the mélange formations of Paleokerasia and Agios Georgios are covered by all studied samples, except for sample 159/PALK. They are basic to intermediate (SiO<sub>2</sub> 50.8-62.2 wt.%), low in magnesium (MgO 1.4-7.8 wt.%) and seem to be basalts and andesites (Table 1, Fig. 2). Sample 275/PALK however, has very high alkali contents (Na<sub>2</sub>O+K<sub>2</sub>O 8.8 wt.%) which classifies the rock as trachyandesite. Sample 159/PALK from the mélange formation of Paleokerasia has higher silica contents and is classified as rhyodacite (Fig. 2). All rocks show calc-alkaline affinities as seen in the La-Y-Nb diagram (Fig. 3), a fact which is further supported by their high Th values.

The studied rocks present subparallel *REE* patterns (Fig. 4) between sample EX12/PALK having the lowest  $\Sigma REE$  values and sample 275/PALK being the highest. *LREE* are enriched compared to *MREE* and *HREE* (20-100 x CN), *MREE* range between 10-70 x CN and *HREE* are even lower, but with flat patterns, ranging between 8-15 x CN. The (La/Sm)<sub>N</sub> and (La/Yb)<sub>N</sub> values range between 2.2-3.3 and 4.3-9.4 respectively. They present very small to significant negative Eu anomalies



Fig. 2. SiO<sub>2</sub> vs. Zr/TiO<sub>2</sub> diagram (Winchester & Floyd 1977) for the volcanic rocks from the mélange formations of Paleokerasia and Agios Georgios in Othris. (Com/Pan) Comendite/Pantellerite; (Sub-AB) Subalkaline basalt; (Alk-Bas) Alkali basalt; (Bas/Trach/Neph) Basanite/Trachyte/Nephelinite

Table 1. Whole-rock major element (wt %) and trace element (ppm) compositions of samples studied—Major elements, Ni, Cr, V, Cu and Zn were measured by XRF, C and S – with LECO instrument. Others were measured by ICP-MS. b.d.l., below detection limit

Sample	129/A.GE	159/PALK	160/PALK	275/PALK	EX12/PALK
Rock type	andesite	rhyodacite	andesite	trachyandesite	basalt
Location	Agios Georgios	Paleokerasia	Paleokerasia	Paleokerasia	Paleokerasia
latitude	N38°57'62"	38°56'19"	38°56'19"	38°56'18"	38°56'16"
longitude	E22°40'36"	22°44'42"	22°44'42"	22°44'52"	22°43'98"
SiO <sub>2</sub>	60.38	66.34	51.57	59.88	47.38
TiO <sub>2</sub>	0.41	0.70	0.66	0.66	0.72
Al <sub>2</sub> O <sub>3</sub>	11.74	15.78	13.54	17.36	13.48
FeO tot	5.80	1.67	6.31	3.46	8.65
MnO	0.08	0.05	0.16	0.07	0.15
MgO	2.58	0.65	7.33	1.38	6.42
CaO	12.21	6.73	10.16	5.47	11.56
Na <sub>2</sub> O	2.09	5.84	4.04	5.13	4.17
K <sub>2</sub> O	b.d.l.	0.08	0.32	3.31	0.33
$P_2O_5$	0.11	0.22	0.18	0.19	0.12
LOI	4.50	2.60	6.40	3.80	6.80
Total	99.90	100.66	100.68	100.72	99.78
Cr	237	197	468	64	601
Ni	43	26	132	27	110
Cu	16	33	32	20	47
Zn	52	44	52	52	66
Rb	b.d.l.	1.3	7.3	79.0	6.0
Sr	43.1	119.6	296.0	423.6	377.2
Y	24.5	20.4	19.1	26.2	12.1
Zr	84.0	110.8	98.1	168.8	45.7
Nb	3.4	5.6	4.2	7.8	2.1
Sb	0.2	0.1	0.1	0.1	0.1
Cs	b.d.l.	0.2	0.1	2.2	1.5
Ba	33.0	36.2	66.2	845.6	102.0
Hf	2.5	3.2	3.0	5.4	1.5
Та	0.5	0.7	0.3	0.8	0.3
Pb	12.7	9.1	7.3	11.4	6.0
Th	4.8	5.9	3.9	12.1	3.1
U	0.6	2.8	1.7	3.2	0.8
La	22.90	17.40	12.50	27.00	7.10
Ce	48.10	38.70	28.50	62.60	15.40
Pr	5.64	4.80	3.39	7.08	2.10
Nd	20.90	18.60	14.90	27.90	8.90
Sm	4.40	4.00	3.50	5.90	2.25
Eu	1.13	1.14	0.92	1.27	0.76
Gd	4.75	3.72	2.95	4.97	2.35
Tb	0.83	0.62	0.64	0.79	0.40
Dy	4.09	3.47	3.20	4.21	2.25
Но	0.72	0.68	0.65	0.87	0.46
Er	2.21	2.04	1.92	2.59	1.28
Tm	0.28	0.30	0.27	0.39	0.20
Yb	1.65	2.08	1.96	2.46	1.22
Lu	0.23	0.30	0.28	0.37	0.19
C tot	0.31	0.22	0.96	0.70	0.90
S tot	0.01	0.01	0.01	0.02	b.d.l.
[Fe]	9.65	5.49	8.49	9.88	10.92
[Mg]	8.49	5.76	20.23	10.56	17.48



diagram

of

Agios

Fig. 4. Chondrite-normalized REE patterns (normalization factors from McDonough & Sun 1995) of the volcanic rocks from the mélange formations of Paleokerasia and Agios Georgios in Othris. The data of the transitional E-MORB Triassic lavas from Othris are according to Tsikouras (2008), Monjoie et al. (2008) and Koutsovitis et al. (2009); of the Middle Triassic calc-alkaline basalts from Koziakas; Glykomilia region according to Magganas et al. (1997) and Pomonis et al. (2004) and of the Middle to Upper Triassic calcalkaline basalts from Lakmon (Pindos region), Gionna (Central Greece) and villages of Platano and Kokkino (Peloponnese region) are according to Pe-Piper & Piper (1991) and Pe-Piper (1998)

 $(Eu_N/Eu^* = 0.72-0.98)$ , which may be due to plagioclase fractionation, changes in  $fO_2$  conditions or crustal contamination of the source. Plagioclase fractionation processes seem more likely to have taken place, since the Eu anomalies increase with decreasing Cr and Ni values. Middle to Upper Triassic calc-alkaline rocks from Lakmon (Pindos region), Glykomilia (Koziakas region), Gionna (Central Greece) and villages of Platano and Kokkino (from the eastern and south-western Peloponnese regions respectively) show similar *REE* patterns as the studied ones from Othris (Pe-Piper & Piper 1991; Pe-Piper 1998; Magganas et al. 1997; Pomonis et al. 2004). In Othris rocks similar LREE enriched patterns are seen in alkaline and transitional E-MORB Triassic lavas (Tsikouras 2008; Monjoie et al. 2008; Koutsovitis et al. 2009). The studied rocks present similar MREE and HREE patterns as the transitional E-MORB lavas, but exhibit higher LREE values and also negative Eu anomalies. The only exception is the sample EX12/PALK with patterns subparallel to the transitional E-MORB lavas and no Eu anomaly. The multi-element patterns (Fig. 5) show relatively high Th and U contents, pronounced negative Nb and Pb anomalies and small to significant negative Ti anomalies. Tantalum chondrite normalized values are



Fig. 5. Primitive mantle-normalized multi-element patterns (normalization factors from McDonough & Sun 1995) of the volcanic rocks from the mélange formations of Paleokerasia and Agios Georgios in Othris. The data of the middle Triassic calc-alkaline basalts from Koziakas, Glykomilia region are according to Magganas et al. (1997) and Pomonis et al. (2004), of the middle to upper Triassic calc-alkaline basalts from Lakmon (Pindos region), Gionna (Central Greece) and villages of Platano and Kokkino (Peloponnese region) are according to Pe-Piper & Piper (1991) and Pe-Piper (1998)

higher than these of Nb, but lower than these of La. The calc-alkaline rocks from the referred localities in the regions of Pindos, Gionna, Koziakas and Peloponnese show similar multielement patterns (Fig. 5) (Pe-Piper & Piper 1991; Magganas et al. 1997; Pomonis et al. 2004).

# Petrographic description and mineral chemistry

The basalts and andesites vary in mineral size from fine to medium grained. They consist of altered phenocrysts which are usually plagioclases, but also clinopyroxenes. Both are subhedral, while plagioclases sometimes show multiple twinning on albite law. The matrix consists mainly of plagioclases, clinopyroxenes and devitrified glass, mostly composed of chlorite. Textures present are ophitic and subophitic, while lath-shaped plagioclases are in some cases orientated forming trachytic textures. Porphyritic and glomeroporphyritic textures have been also recognized. Minerals such as chlorite, prehnite, calcite and white mica appear in all rocks, showing that they underwent low grade oceanic metamorphism. The low grade metamorphism is also confirmed by the absence of secondary hornblende. Accessory minerals include spinel, magnetite, ilmenite, titanite, quartz, calcite, apatite and zircon. Small amygdales of calcite and chlorite appear in spherical form. Trachyandesite from Paleokerasia differs from the basalts and andesites in having larger phenocrysts, additionally containing alkali feldspars and in some cases having zoned plagioclases. The rhyodacite mainly consists of quartz and plagioclases. Plagioclase phenocrysts are altered, subhedral, prismatic or granular albites, while the matrix consists mainly of albite, chlorite and calcite. The rock is crosscut by secondary quartz veins.

Representative mineral chemistry data of clinopyroxenes, feldspars and spinels are shown in Tables 2 and 3. Clinopyroxenes are augites with intermediate MgO contents (Mg<sup>#</sup> 72.4-86.9) and low TiO<sub>2</sub> contents with Ti/Al

ratio values ranging between 0.01-0.17. Cr and Ni have very low concentrations and it is pointed that the Mg<sup>#</sup> values of phenocrysts are almost the same as the ones within the matrix. Albites are present within all samples. The trachyandesite additionally contains plagioclases of very wide compositional range (An<sub>26.7-60.1</sub>) and potassic feldspars (Or<sub>66.1</sub>). The above-mentioned plagioclase phenocrysts are chemically zoned with cores having slightly higher An values than in their rims (regular continuous zoning). Spinels are characterized as aluminium chromites with relatively high Cr<sub>2</sub>O<sub>3</sub> (Cr<sup>#</sup> 79.8-81.3) and low Al<sub>2</sub>O<sub>3</sub> ranging between 8.57-9.27 wt%.

# Discussion

## *Geotectonic environment*

The studied rocks are plotted on the Th/Yb vs. Nb/Yb diagram (Fig. 6) above the MORB-OIB mantle array indicating that they are affected by subduction related processes. They also show that sediment input may have contaminated the mantle source or perhaps the upwelling magma before erupting. Noteworthy is the fact that they also plot within the fields formed by Middle to Upper Triassic calcalkaline volcanic rocks from Pindos and Peloponnese (Pe-Piper & Piper 1991; Pe-Piper 1998). Alkaline and transitional E-MORB basalts of Othris are also plotted for comparison (Fig. 6). The Nb/Th ratio has been used by researchers (e.g. Fang & Niu 2003) to investigate the effect of subduction processes in the formation of volcanic rocks. Values lower than '4' characterize arc related rocks, while N-MORB lavas have average values '19.4', E-MORB lavas '13.8' and OIB '12' (Sun & Mcdonough 1989). Nb/Th values for the studied rocks range between 0.64-1.42 which are significantly lower than '4' confirming that they were probably affected by subduction related processes. The multielement patterns of the studied rocks (Fig. 5), as mentioned, show relatively high Th and U contents, pronounced negative Nb and positive

Sample		160/PALK			275	/PALK	
Analysis No	1	9	8	1ex	4	14	23
	Phenocryst	Phenocryst		Phenocryst			
SiO <sub>2</sub>	52.94	52.42	52.22	52.37	52.17	52.53	52.52
TiO <sub>2</sub>	0.26	0.27	0.26	0.41	0.00	0.00	0.56
$Al_2O_3$	1.66	2.07	1.86	2.09	3.17	1.94	2.32
FeO <sup>t</sup>	6.54	5.85	6.30	9.67	9.07	8.83	8.77
MnO	0.20	0.20	0.17	0.36	0.19	0.00	0.00
MgO	17.73	17.70	17.39	14.22	14.52	16.31	15.01
CaO	19.44	19.97	19.31	20.61	20.53	19.26	19.92
Na <sub>2</sub> O	0.16	0.17	0.16	0.12	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.01	0.04	0.00	0.00	0.00
$Cr_2O_3$	0.27	0.62	0.21	0.64	0.25	0.00	0.00
NiO	0.06	0.03	0.05	0.00	0.00	0.00	0.00
Total	99.26	99.29	97.93	100.54	99.91	98.87	99.10
Si	1.951	1.928	1.949	1.947	1.941	1.961	1.968
<sup>iv</sup> Al	0.049	0.072	0.051	0.053	0.059	0.039	0.032
<sup>vi</sup> Al	0.023	0.018	0.031	0.038	0.080	0.046	0.071
Ti	0.007	0.007	0.007	0.011	0.000	0.000	0.016
Fe <sup>3+</sup>	0.015	0.033	0.010	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.186	0.147	0.187	0.301	0.282	0.276	0.275
Mn	0.006	0.006	0.005	0.011	0.006	0.000	0.000
Mg	0.974	0.971	0.968	0.788	0.805	0.908	0.839
Ca	0.767	0.787	0.772	0.821	0.819	0.770	0.800
Na	0.011	0.012	0.011	0.009	0.000	0.000	0.000
Κ	0.000	0.000	0.000	0.002	0.000	0.000	0.000
Cr	0.008	0.018	0.006	0.019	0.007	0.000	0.000
Ni	0.002	0.001	0.001	0.000	0.000	0.000	0.000
Total	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Mg#	0.84	0.87	0.84	0.72	0.74	0.77	0.75
En	50.0	49.9	49.8	41.0	42.1	46.5	43.8
Fs	10.7	9.6	10.4	16.2	15.1	14.1	14.4
Wo	39.4	40.5	39.8	42.8	42.8	39.4	41.8
Analytical					~		
facility	WDS	WDS	WDS	EDS	EDS	EDS	EDS

Table 2. Representative microprobe analyses of clinopyroxenes from calc-alkaline volcanic rocks of Othriscalculated for 6 oxygens

volcanic rocks of Othris. F	
Table 3. Representative microprobe feldspar and spinel analyses from calc-alkaline           spinels for 4	pinets for 4

spinels for 4											
			Feldspars	Dars					Spinels		
Sample	160/PALK			275/PALK	K		159/PALK	sample	10	160/PALK	
Analysis No	2		7	13	5ex	3	4	Analysis No	L	6	11
Mineral	albite		oligoclase	andesine	labradorite	K-feldspar	albite				
$SiO_2$	67.94		60.47	54.95	54.13	66.26	67.39	$SiO_2$	0.04	0.80	0.36
$TiO_2$	0.00		0.00	0.00	0.01	0.37	0.01	TiO <sub>2</sub>	0.33	0.41	0.32
$Al_2O_3$	20.12		23.68	29.21	27.88	19.13	19.33	$Al_2O_3$	8.57	9.09	9.27
$\mathrm{Fe_2O_3^t}$	0.27		0.56	0.00	0.54	0.16	0.06	$FeO^{t}$	27.15	27.46	27.27
MnO	0.02		0.00	0.00	0.00	0.15	0.00	MnO	0.48	0.00	0.00
MgO	0.01		0.00	0.00	0.08	0.00	0.00	MgO	7.82	8.08	8.02
CaO	0.25	1.05	5.39	11.52	11.65	0.38	0.47	CaO	0.04	0.10	0.16
$Na_2O$	11.40		7.51	4.23	4.70	3.08	11.54	$Na_2O$	0.00	0.16	0.00
$K_2O$	0.23		1.01	0.00	0.39	9.75	0.03				
$Cr_2O_3$	0.00		0.00	0.00	0.00	0.00	0.00	$Cr_2O_3$	55.40	54.68	54.64
NiO	0.01		0.00	0.00	0.00	0.00	0.01	NiO	0.08	0.00	0.00
Total	100.24		98.62	99.91	99.36	99.28	98.85	Total	97.71	99.25	98.85
Si	2.966		2.731	2.470	2.467	3.000	2.982	Si	0.001	0.026	0.012
Al	1.035		1.261	1.547	1.497	1.021	1.008	Al	0.340	0.351	0.364
Ti	0.000		0.000	0.000	0.000	0.013	0.000	Ti	0.008	0.010	0.008
$\mathrm{Fe}^{3+}$	0.013		0.029	0.000	0.028	0.003	0.003	$\mathrm{Fe}^{3+}$	0.162	0.143	0.145
								${ m Fe}^{2+}$	0.606	0.610	0.616
Mn	0.001		0.000	0.000	0.000	0.006	0.000	Mn	0.014	0.000	0.000
Mg	0.001		0.000	0.000	0.005	0.000	0.000	Mg	0.392	0.394	0.398
Ca	0.011		0.261	0.555	0.569	0.019	0.022	Ca	0.001	0.004	0.006
Na	0.965		0.658	0.369	0.415	0.270	0.990	Na	0.000	0.010	0.000
K	0.013		0.058	0.000	0.022	0.563	0.002				
Cr	0.000		0.000	0.000	0.000	0.000	0.000	Cr	1.474	1.414	1.437
Ni	0.000		0.000	0.000	0.000	0.000	0.000	Ni	0.002	0.000	0.000
Total	5.006	4.982	4.997	4.941	5.003	4.894	5.009	Total	3.000	2.962	2.985
An	1.2		26.7	60.1	56.5	2.2	2.2	Mg#	39.3	41.0	40.6
Ab	97.5		67.3	39.9	41.2	31.7	97.6	Cr#	81.3	80.1	79.8
Or	1.3		6.0	0.0	2.2	66.1	0.2				
Analytical facility	MDS	WDS	EDS	EDS	MDS	EDS	MDS	Analytical facility	MDS	EDS	EDS
								•			



Fig. 6. Plot of Th/Yb vs. Nb/Yb with the points of the studied rocks and for comparison the fields of Triassic alkaline and intermediate E-MORB basalts of Othris (according to Tsikouras 2008; Monjoie et al. 2008 and Koutsovitis et al. 2009), calc-alkaline basalts from Koziakas, Glykomilia region (according to Magganas et al. 1997 and Pomonis et al. 2004) and from Peloponnese (villages of Platano and Kokkino) (Pe-Piper & Piper 1991 and Pe-Piper 1998). The MORB-OIB is according to Pearce (1983)

Pb anomalies and small to significant negative Ti anomalies. All these features correspond to rocks formed in a subduction related environment (Pearce & Peate 1995). Clinopyroxene analyses are plotted in the SiO2-TiO2-Na2O diagram (Fig. 7) and fall within the boninite, island arc and back arc basin fields, which are all related to subduction processes. Spinel chemistry seems to agree with the previous conclusions as seen by their TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents (Fig. 8). These striking evi-dences favour formation of the studied rocks in a subduction environment. However. some researchers (e.g. Bebien et al. 1980; Dixon & Rutherford 1983; Dixon & Robertson 1993; Robertson et al. 1990; Pe-Piper 1998) mention that during the Triassic the mantle might have been enriched by inherited hydrous fluids from a Hercynian subduction event, which occurred prior to the break up of the Gondwana continental margin. Such a scenario cannot be excluded as an event which may have additionally hydrated the mantle, but it cannot explain the striking subduction features printed on the calc-alkaline volcanic rocks. Furthermore it would be difficult for a heterogeneous mantle to produce both rift related and subduction related volcanic rocks.

### **Petrogenetic implications**

Alkaline rocks in the Othris and in other regions in Greece, such as Evia (Simantov & Bertrand 1987; Robertson 1991; De Bono 1998) and Pindos (Jones & Robertson 1991) with OIB geochemical characters are considered to represent the volcanic rocks formed in an infant oceanic basin which could have possibly formed seamounts. Alkaline OIB volcanism has been accounted to melting of an



enriched mantle source in high depths with garnet as a component (Pearce & Parkinson 1993). This volcanic activity could have enriched the fertile upper mantle with LREE. As observed in the Th/Yb vs. Nb/Yb diagram (Fig. 6) the studied rocks seemed to have either been affected by sediment contamination processes or could have been simply formed by the addition of a subduction component in the transitional E-MORB volcanism. Transitional volcanism could have occurred with partial melting of the LREE enriched mantle source and could justify its E-MORB character. A latter stage subduction event would then change the E-MORB volcanism to calcalkaline one. Sample EX12/PALK presents almost the same chondrite normalized REE values as the transitional E-MORB lavas with

Fig. 7. SiO<sub>2</sub>-TiO<sub>2</sub>-Na<sub>2</sub>O diagram for discriminating clinopyroxenes. Fields drawn according to Beccaluva al. (1989).et Abbreviations: within oceanic plate basalts (WOPB), normal (N-) and enriched (E-) mid-ocean ridge basalts (MORB), island-arc tholeiites (IAT) and intraoceanic back and fore-arc regions (BA-A). Analyses from Table 2

the lowest  $\Sigma REE$  values (Fig. 4) (Tsikouras 2008; Monjoie et al. 2008; Koutsovitis et al. 2009) indicating that calc-alkaline and E-MORB volcanism may had been closely related. The absence of significant negative Ta anomalies such as the ones observed for Nb in the multi-element patterns (Fig. 5) further weaken the scenario of crustal contamination processes, however this possibility cannot be excluded. Melting is assumed to have occurred in the spinel stability field (13-25 kbar) since clinopyroxene chemistry shows that the rocks formed probably formed under medium to slightly high pressure conditions (Fig. 9). The range of [Fe] values (5.5-10.9) and of Cr contents (64-601 ppm) (Table 1) indicates that fractional crystallization processes affected the rocks, but not to very high degrees. [Fe] values



Fig. 8.  $TiO_2$  vs.  $Al_2O_3$  (in wt.%) diagram of spinels. Fields from continent flood basalts (LIP), ocean island basalts (OIB), mid-ocean ridge basalts (MORB), island-arc volcanics (Arc) after Kamenetsky et al. (2001). Analyses from Table 3

are compositionally corrected Fe abundances in cation mole percent using the third equation of Ford et al. (1983), which is based on compositionally corrected olivine-melt Kds for FeO. As referred, plagioclase fractionation processes seem likely to have taken place since the Eu anomalies increase with decreasing Cr and Ni values.

Taking the above observations under consideration we assume a hypothetical mantle source 'M' which has almost the same *MREE* and *HREE* values as the one of the FMM (Fertile MORB Mantle - Pearce & Parkinson 1993), but enriched in *LREE*. This enrichment is attributed to the enrichment of the upper mantle from the earlier OIB volcanic activity. For *REE* modelling of the studied samples we use the non modal batch melting and fractional crystallization equations of Shaw (1970). The mantle source is spinel lherzolite, since we assumed a fertile mantle source and melting in the spinel stability field (mineral proportions and melt mode proportions are

 $ol_{0.53}$ + $opx_{0.27}$ + $cpx_{0.17}$ + $sp_{0.03}$  and

ol<sub>0.06</sub>+opx<sub>0.28</sub>+cpx<sub>0.67</sub>+sp<sub>0.11</sub> respectively,

Kinzler 1997). Partition coefficients are from McKenzie & O'Nions (1991, 1995). It seems that the less fractionated sample 'EX12/PALK (lowest  $\Sigma REE$  values, almost no negative Eu anomalies and highest Cr contents) can be modelled with 15% anhydrous melting of the hypothetical mantle source 'M' (Fig. 10). It should be noted that the studied rocks were formed in a subduction environment, which apparently involves the effect of hydrous fluids, so that the calculated melting degree is regarded as the highest possible. The rest of the samples seemed to have formed by variable degrees of fractional crystallization which may reach up to 25%.



Fig. 10. *REE* petrogenetic modelling of the studied calc-alkaline volcanic rocks, using the hypothetical source 'M'. The FMM (Fertile MORB Mantle) is also plotted for comparison. Calculations are done using the non modal batch melting and fractional crystallization equations of Shaw (1970). The mantle source is spinel lherzolite. Partition coefficients are from McKenzie & O'Nions (1991, 1995) and normalizing values are from McDonough & Sun (1995). Transitional E-MORB Triassic lavas from Othris are shown for comparison (according to Tsikouras 2008; Monjoie et al. 2008 and Koutsovitis et al. 2009)

# Conclusions

The studied volcanic rocks from the mélange occurrences of Paleokerasia and Agios Georgios in South Othris region occur usually as pillow lavas of basaltic, andesitic and trachyandesitic composition and in fewer cases as rhyodacites. All studied rocks have calcalkaline geochemical affinities. They show very similar major element contents as well as *REE* and multi-element normalized patterns with calc-alkaline rocks from Lakmon (Pindos region), Glykomilia (Koziakas region), Gionna (Central Greece) and villages of Platano and Kokkino (from the eastern and southwestern Peloponnese regions respectively) dated as Middle to Late Triassic. This indicates that the studied rocks may have been produced from the same Middle to Late Triassic calc-alkaline volcanic episode. The volcanic activity seems to have occurred in a subduction environment as shown by geochemical and mineral chemistry data. The geochemical data which point to this conclusion are the very low Nb/Th ratio values (0.64-1.42) and the multi-element patterns which show pronounced negative Nb and positive Pb anomalies as well as small to significant negative Ti anomalies. Additionally mineral chemistry data from clinopyroxenes and spinels show that the volcanic rocks formed in an island-arc setting. These conclusions may support the formation of the calc-alkaline volcanic rocks to a different geodvnamic setting rather than the ones referred by other researchers (e.g. Bebien et al. 1980; Dixon & Rutherford 1983; Dixon & Robertson 1993; Robertson et al. 1990; Pe-Piper 1998) who state that during the Triassic no subduction occurred, but the mantle was enriched by inherited hydrous fluids from a Hercynian subduction event, occurring prior to the break up of the Gondwana continental margin. Though, this event cannot be totally excluded and may have played also a role in hydrating the mantle additionally, it cannot explain the remarkable subduction features. This volcanic activity may indicate a change in an otherwise rift related environment, recorded by the alkaline and transitional, OIB and MORB related rocks. The absence of strong negative Ta anomalies, compared to intense Nb anomalies in the multi-element normalised patterns, weakens the possibility for sediment addition processes to have played a significant role, but it cannot be excluded. Taking this into consideration it seems more likely that subduction processes, which led to the formation of the calc-alkaline lavas, took place in an intraoceanic environment, without excluding the possibility that they are related with a more mature arc environment, influenced by a nearby lithospheric continental crust. An isotopic geochemistry study is anticipated in the short future to further investigate these processes. Clinopyroxene chemistry reveals that rocks were formed under moderate to high pressure conditions, expected for a mantle source in the spinel stability field. For the petrogenetic modelling of the *REE* we used a fertile mantle source enriched in *LREE* (mantle source 'M'), due to previous OIB magmatism. Results show that the studied rocks could have been produced with 15% anhydrous partial melting of the mantle source 'M' and variable degrees of fractional crystallization reaching up to 25%.

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