

## COMPARATIVE GEOCHEMICAL STUDY OF THE TRIASSIC TRACHYANDESITES OF GLYKOMILIA AND ALKALI BASALTS FROM THE KOZIAKAS OPHIOLITE MÉLANGE (W. THESSALY): IMPLICATIONS FOR THEIR ORIGIN

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### ABSTRACT

The Triassic Glykomilia trachyandesites of the Koziakas mountain range (western Thessaly) are parts of the oldest volcanic series in continental central Greece. Rock fragments and blocks of pillowed alkali basalts, which are dispersed into the Koziakas ophiolite mélange, display similar sub-parallel chondrite-normalized trace and rare earth element patterns to the trachyandesites, suggesting a common origin. However, the Glykomilia trachyandesites are more differentiated than the Koziakas alkali basalts, which display a different petrogenetic evolution from the basalts occurring in the Koziakas Ophiolite Unit. REE patterns and discrimination diagram plots reveal significant similarities to Triassic volcanic rocks from the Hellenides, suggesting also a VAB signature for the Glykomilia trachyandesites and a WPB affinity for the alkali basalts. Partial melting of a LILE-enriched hydrous mantle under spreading conditions is suggested to give rise to Glykomilia trachyandesites. This partial melting episode was probably induced by the uplift of an OIB-type mantle plume, which subsequently produced the WPB alkali basalts of the Koziakas ophiolite mélange. The close association of both the Glykomilia trachyandesites and the Koziakas alkali basalts with cherts lead to the hypothesis of eruption in a deep rift basin.

### 1 INTRODUCTION

In Greece, the oldest volcanic rocks associated with the Alpine orogenesis are of Palaeozoic to Early Mesozoic age. Hercynian (c. 300 Ma) subduction of Palaeotethys at an Andean-type margin (Finger & Streyer, 1990) was followed by Late Carboniferous, Permian and Triassic continental rifting of northeastern Gondwana, eventually leading to the creation of a mosaic of late Triassic to Jurassic small Red Sea-type ocean basins. The main rifting event took place in early to mid-Triassic times (Mountrakis et al., 1983; Robertson et al., 1991). Upper Scythian and Lower Anisian submarine lavas are usually associated with red limestones and cherts. Volcanic activity in places continued to the late Triassic (Pe-Piper, 1998).

The petrographic and geochemical data reported so far on the Triassic volcanic rocks from different outcrops of both external (Gavrovo-Tripolis and Pindos Units) and intermediate (Western Thessaly, Parnassos, Maliac and Eastern Greece Units) zones of Hellenides, indicate a wide compositional spectrum with rocks ranging from calc-alkaline to transitional alkaline and alkaline (e.g., Ardaens, 1978; Ferrière, 1982; Pe-Piper, 1982, 1983; Pe-Piper and Panagos, 1989; Pe-Piper and Mavronichi, 1990; Magganas et al., 1997; Capedri et al., 1997).

The Triassic volcanic rocks of the Koziakas mountain range (western Thessaly) are parts of the oldest volcanic series, associated with the Alpine orogenesis, in continental central Greece. In this study we attempt a geochemical comparison between Triassic trachyandesites found at the northern part of the Koziakas range and alkali basalts, found into the ophiolitic mélange of the Koziakas ophiolite. Our aim is to investigate their petrogenetic evolutions and the tectonic regime of their origin.

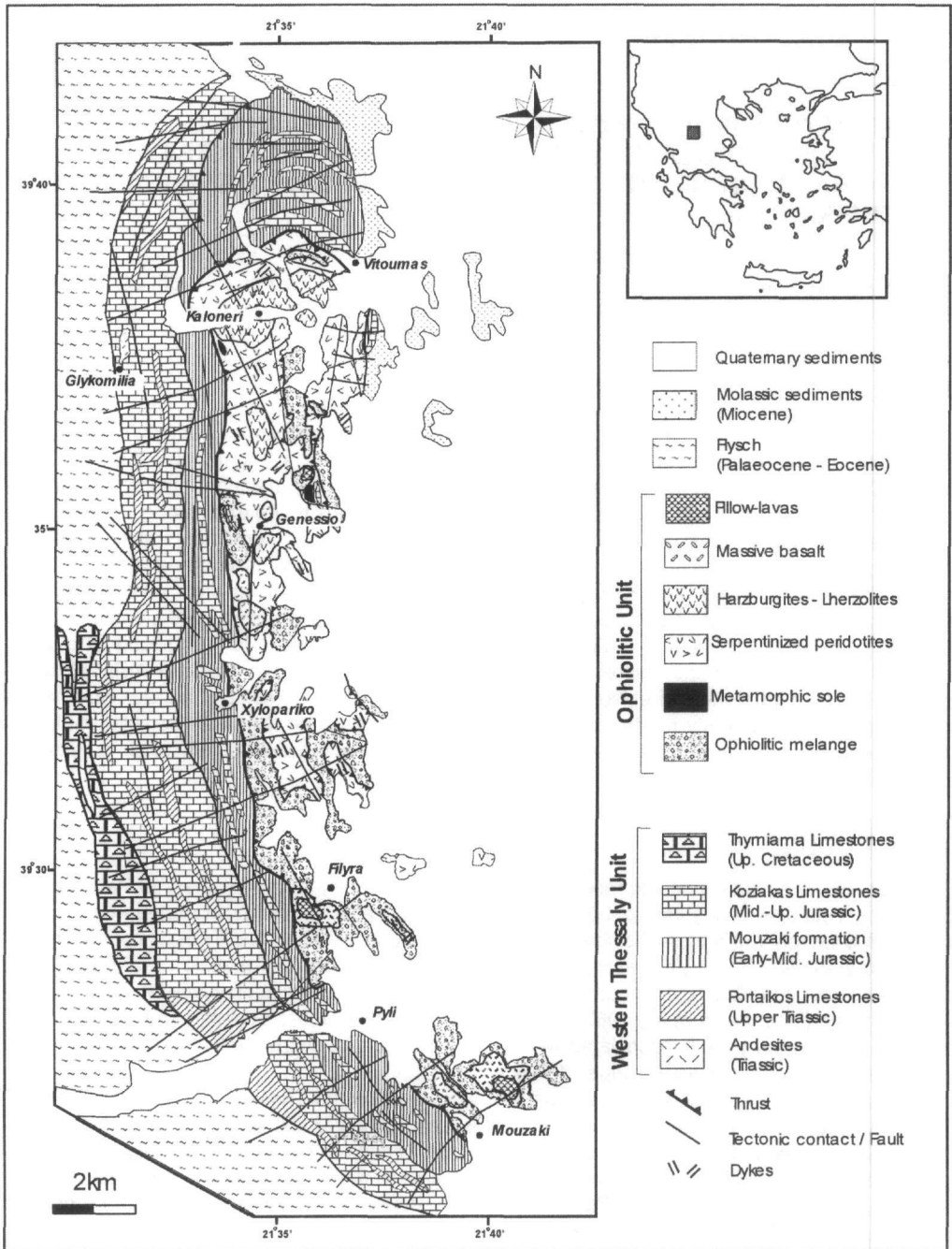


Figure 1. Geological map of the Koziakas ophiolite complex.

## 2 FIELD OCCURRENCE

The Koziakas ophiolite belongs to the Western Thessaly Unit – W.T.U. (Papanikolaou & Sideris, 1979), a series of sedimentary and volcanic rocks of Upper Triassic – Eocene age. Extensive field-

work in the ophiolitic complex of Koziakas focused on the distribution and mode of development of the ophiolitic rocks and produced a detailed geological map (Fig. 1).

The basement of the Koziakas ophiolite is represented by Alpine-type sedimentary rocks of the W.T.U., which occurs in the western part of the Koziakas mountain range. The Portaikos limestones of Upper Triassic age, comprises the lower member of the W.T.U. These rocks are overlain by the Mouzaki formation, which consists of medium-bedded sequences of cherts, siltstones and oolitic limestones of Lower – Middle Jurassic age. The Koziakas limestone formation is composed of oolitic limestones of Middle-Upper Jurassic age. It is tectonically overlain by the Mouzaki formation and locally underlain the Thymiama limestones of Upper Cretaceous age (indicated by the occurrence of microfossils). Finally, both the Koziakas and the Thymiama limestones are thrust over the upper part of the W.T.U., consisting of Palaeocene-Eocene flysch, which is transitional to the Pindos flysch (Papanikolaou and Sideris, 1979; Lekkas, 1991).

The Koziakas ophiolitic complex is an uncompleted ophiolite unit with an ophiolitic mélange at its base. The ophiolite mélange is thrust over the W.T.U. while it is also in thrust contact with the overlying ophiolitic unit. It comprises a chaotic, multicoloured mixture of rock-fragments of variable lithology, shape and size in the form of tectonic blocks. These blocks include serpentinites, peridotites, gabbros, dolerites, pillow-lavas, amphibolites, radiolarites, limestones, argillitic schists and sandstones. Small outcrops of sub-ophiolitic metamorphic rocks are thrust over the ophiolite mélange. They are in tectonic contact with the overlying ophiolitic unit consisting a metamorphic sole. The lower parts of the dismembered ophiolite unit consists of serpentinites, serpentinitized peridotites (harzburgites and lherzolites) intruded by gabbroic, rodingitized gabbro and plagiogranitic veins up to 0.5 m width (not shown on the map). Its upper parts include small outcrops of olivine gabbro, dolerites and pillow lavas interlayered with Mn-rich radiolarites (Pomonis, 2003).

The Koziakas alkali basalts were detected into the ophiolitic mélange (Fig. 1) only, as dispersed fragments, locally associated with red limestones fragments of Upper Triassic age (Portaikos limestones) and radiolarites. In cases, there are fragments of pillow alkali basalts associated with radiolarites, the later following all their surface anomalies. The alkali basalts are usually purplish with amygdules, or blue-grey when fresh. Few samples display amygdules.

The Triassic trachyandesites occur in the NW part of the Koziakas mountain range, near Glykomilia village (Fig. 1). They form small lava flows, about 50m in thickness concordantly associated with Norian conodonts bearing red limestones (Portaikos limestones) and radiolarites (Magganas et al., 1997). The colour of these volcanics is light brown to grey-beige, while in fractured areas, due to oxidation, it is dark brown to black. They show porphyritic structure with well-observed phenocrysts of feldspars and pyroxenes, with a size of 2-3 mm and rarely up to 1cm.

### 3 PETROGRAPHY

The Koziakas alkali basalts display a range of textures from aphyric and variolitic to plagioclase-porphyritic. When texture is porphyritic, the proportion of phenocrysts to groundmass is variable. Subhedral laths of plagioclase and interstitial clinopyroxene, are settled in an intergranular to intersertal groundmass with microlites of plagioclase and clinopyroxene. The plagioclase and clinopyroxene crystals present variable alteration or replacement signs by secondary minerals. Locally feldspar crystals are almost completely altered to calcite. Fe-Ti oxides are the opaque phases present and they have a strong association with the altered crystals. Secondary minerals due to low-grade ocean metamorphism found: quartz, albite, epidote, chlorite, pumpellyite, calcite, hematite, titanite and actinolite. Some samples display calcite-chlorite-filled amygdules. Carbonate veins cutting all mineral phases have also been seen.

The Glykomilia trachyandesites are unusually fresh with porphyritic texture (~40 vol.% phenocrysts). Local accumulation of feldspars and pyroxenes phenocrysts creates a glomeroporphyritic structure. Their groundmass is hypocrySTALLINE, composed mainly of brownish glass. The feldspars are weakly altered to smectite and celadonite, and consist mainly of plagioclase, whereas in smaller amounts K-feldspars occur. The celadonite, however, might well represent altered pyroxene inclusions within the feldspars. Twinning and zoning are common in all feldspars. Other alteration products are: calcite, albite, pumpellyite, Fe-oxides, quartz, chlorite and rarely epidote and

white mica. Locally, chlorite replaces partly or totally phenocrysts of pyroxenes and feldspars. Veinlets of chlorite, calcite and quartz, cross cut the rock.

#### 4 ANALYTICAL TECHNIQUES

Whole-rock major element analyses were performed using a JY24 Sequential Spectrometer (ICP-AES), while Si was determined by X-ray fluorescence, using a Spectro Analytical X-Lab 2000 XRF spectrometer. Detection limits for most elements were less than 0.005 wt.% in the sample and analytical errors characteristically varied from 2% to 5%, depending on the element determined and its concentration.

Trace and Rare Earth Elements (REE) were determined on totally digested samples by inductively coupled plasma-mass spectrometry (ICP-MS) using a VG Elemental Plasma Quad II, following techniques described in Bailey et al. (1993) and Lewis et al. (1997). Detection limits were generally sub ppb in solution, equivalent to sub ppm levels in rock samples, taking into account dilution factors. Precision varied from 5 to 10%, depending on the element determined and its concentration.

All analyses were performed at the University of Bristol, Department of Earth Sciences.

#### 5 GEOCHEMISTRY

Major-, trace- and rare-earth element analyses of representative samples from the Koziakas alkali basalts and trachyandesites are reported in Table 1. Loss on ignition (L.O.I.), which is generally considered as an index of alteration, is rather low in the analyzed samples (with few exceptions mainly in alkali basalts with about 3-6.9). However, studies of low-temperature, seawater-dominated alteration of rocks have shown that the mobility of several elements is affected by seawater interaction (e.g., Seyfried & Mottl, 1982; Alt et al., 1986; Lecuyer et al., 1990). Besides, the alteration seems to have affected the potassium concentration of Glykomilia volcanic rocks, which shows, in comparison with many other elements, a wider range from 3.94% wt. up to 5.33% wt. Thus, in order to constrain on the petrogenesis of these lavas, we based our investigation mostly on the immobile elements.

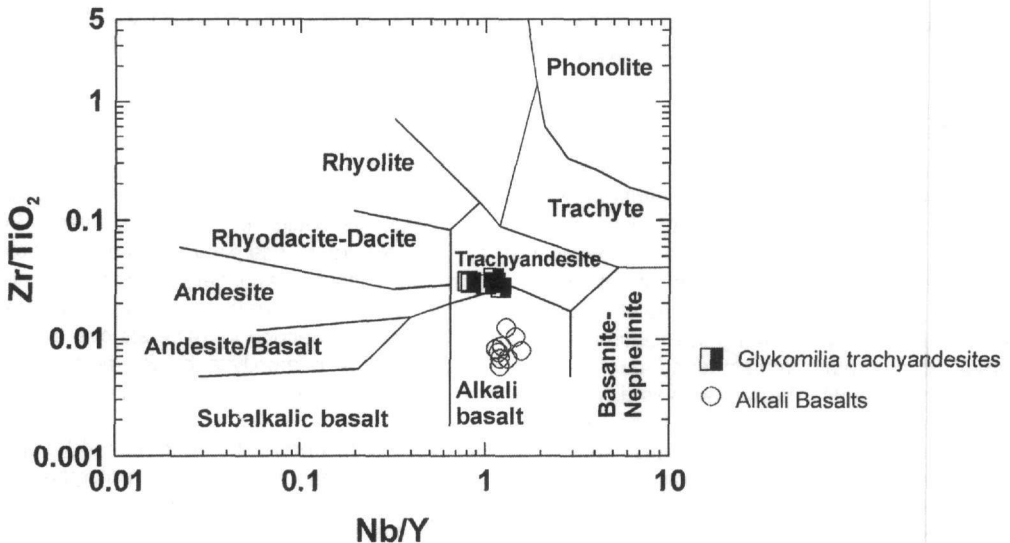


Figure 2.  $Zr/TiO_2$  vs  $Nb/Y$  plot of Winchester and Floyd (1977) for the Koziakas alkali basalts and Glykomilia trachyandesites.

Table 1. Geochemical analyses of representative trachyandesites and alkali basalts from the Koziakas mountain range (- :below detection limit, \*:not determined).

**Major Elements (%wt)**

	<b>Alkali Basalts</b>				<b>Trachyandesites</b>			
	<i>F17</i>	<i>F38b</i>	<i>A176</i>	<i>A177</i>	<i>GL7</i>	<i>GL20</i>	<i>GL21</i>	<i>GL23</i>
SiO <sub>2</sub>	45.22	46.53	46.83	47.36	69.51	65.82	66.68	65.34
TiO <sub>2</sub>	1.30	1.57	1.57	1.41	0.68	0.69	0.61	0.70
Al <sub>2</sub> O <sub>3</sub>	16.97	17.27	15.34	16.83	13.64	14.40	14.07	14.76
Fe <sub>2</sub> O <sub>3</sub> <sup>†</sup>	8.32	7.94	8.52	8.97	3.30	4.18	4.59	4.44
MnO	0.14	0.12	0.14	0.22	0.05	0.08	0.17	0.10
MgO	4.90	5.90	5.91	4.06	1.24	1.92	2.05	2.01
CaO	11.16	10.46	11.16	11.87	2.22	3.05	2.52	1.42
Na <sub>2</sub> O	4.26	4.23	5.03	5.44	2.88	3.98	4.21	3.81
K <sub>2</sub> O	0.21	0.14	0.12	0.33	4.46	3.94	3.98	5.33
P <sub>2</sub> O <sub>5</sub>	0.21	0.27	0.30	0.24	0.13	0.27	0.24	0.26
LOI	6.89	5.59	4.60	3.05	1.96	1.00	0.90	1.70
<b>Total</b>	<b>99.58</b>	<b>100.02</b>	<b>99.52</b>	<b>99.78</b>	<b>100.07</b>	<b>99.32</b>	<b>100.02</b>	<b>99.86</b>

**Trace Elements (ppm)**

V	267	252	360	276	81	116	107	113
Cr	350	300	149	243	38	30	27	31
Co	30	26	-	17	*	*	*	*
Cu	66	75	-	39	*	*	*	*
Ni	138	125	231	135	25	32	21	27
Zn	84	60	-	72	*	*	*	*
Rb	4	-	2	-	114	113	128	129
Sr	224	164	159	80	194	268	255	171
Y	27	21	19	24	9	8	9	8
Zr	96	104	116	121	187	205	196	199
Nb	27	36	34	44	11	9	10	8
Ba	50	54	40	26	595	544	681	702
Sc	29	34	29	28	11	21	27	18
Hf	3	3	3.2	3.2	5	5	4	5
Ta	2	2	4.9	2.7	1	1	2	1
Th	2.7	2	4.8	4.2	12	12	13	13
U	0.8	1	-	1.1	*	*	*	*

**Rare Earth Elements (ppm)**

La	22	28	33	33	30	34	35	44
Ce	41	53	33	60	63	66	66	58
Pr	5	6	9	7	7	10	11	16
Nd	20	23	24	25	26	29	27	41
Sm	4.40	4.20	4.98	4.80	4.70	5.76	5.78	8.29
Eu	1.30	1.37	1.47	1.40	1.00	1.14	1.10	1.73
Gd	4.90	4.70	6.23	4.70	4.80	7.06	7.22	9.93
Tb	0.80	0.70	0.65	0.80	0.60	0.66	0.63	0.86
Dy	4.60	3.70	4.27	4.20	3.20	3.80	3.68	5.42
Ho	0.90	0.70	0.73	0.80	0.70	0.71	0.70	0.89
Er	2.90	2.40	2.14	2.50	2.20	2.11	1.89	2.71
Tm	0.46	0.33	0.29	0.37	0.31	0.23	0.29	0.35
Yb	2.80	2.00	1.87	2.30	1.90	1.92	2.16	2.62
Lu	0.43	0.33	0.29	0.36	0.32	0.27	0.35	0.38

According to Zr/TiO<sub>2</sub> vs. Nb/Y diagram (Winchester & Floyd, 1977, Fig.2), which uses immobile elements only, the analyzed volcanic rocks from Glykomilia plot in the field of trachyandesite, whereas the analyzed volcanic rocks from the Koziakas ophiolitic mélange are classified as alkali basalts. The alkali basalts display higher values in TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub><sup>t</sup>, MgO, CaO and Na<sub>2</sub>O and lower SiO<sub>2</sub> and K<sub>2</sub>O values relative to trachyandesites. On the other hand, the high Si and K contents indicate a transitional alkaline geochemical character for the Glykomilia lavas.

The low MgO/FeO<sup>t</sup> ratio (0.38-0.48) of Glykomilia lavas, relative to alkali basalts (0.41-0.88) indicates a more evolved geochemical character for the trachyandesites. Moreover, the trachyandesites display higher Th/La (0.29-0.40), Th/Yb(4.85-6.32), Th/Ta(7.56-19.67) and La/Nb(2.73-5.46) incompatible element ratios relative to alkali basalts (Th/La:0.07-0.14, Th/Yb:0.96-2.57, Th/Ta:0.84-1.55, La/Nb:0.75-0.98).

Rare earth element patterns of both rock types normalized to chondrite, are plotted in Figure 3. In this figure the patterns of alkali basalts are represented for comparison by an envelope, which outlines their maximum and minimum normalized REE values. The Glykomilia trachyandesites characterized by a strong enrichment in LREE and slightly fractionated HREE ((Ce/Yb)<sub>N</sub>:5.35-3.79). Similar REE profiles present the Koziakas alkali basalts with slightly lower LREE values ((Ce/Yb)<sub>N</sub>:3.75-7.72) relative to trachyandesites. Moreover, both rock types display subparallel fractionated HREE ((Tb/Yb)<sub>N</sub>:1.37-1.83). The well pronounced negative Eu anomaly of Glykomilia trachyandesites indicates rather plagioclase separation.

## 6 DISCUSSION

As evidenced by the overall geochemical features, the petrogenetic evolution of Glykomilia trachyandesites is related with this of the alkali basalts from the Koziakas ophiolitic mélange. Their relatively low MgO/FeO<sup>t</sup> ratio in association with the low to very low Cr and Ni values, suggest that they were formed by fractional crystallization of mafic phases.

The high Th/La, Th/Yb, Th/Ta and La/Nb ratios of Glykomilia trachyandesites, which are higher than the Koziakas alkali basalts is an evidence that trachyandesites probably underwent significant chemical interaction with a continental crust, or a subducted slab activity is involved to their genesis. These ratios are higher than in mantle-derived magmas unaffected by crust interaction. Analogous geochemical signatures present the Triassic volcanic rocks from Vardoussia and Argolis (Capedri et al., 1997). On the other hand, the above incompatible element ratios are lower in the Koziakas alkali basalts (<1) and analogous to those from basalts unaffected by crust contamination (Pearce, 1982). The absence of a "crustal signature" in the Koziakas alkali basalts is consistent with either emplacement onto an ocean floor, or intrusion through the continental crust via rapid ascent that prevented extensive differentiation and crustal contamination.

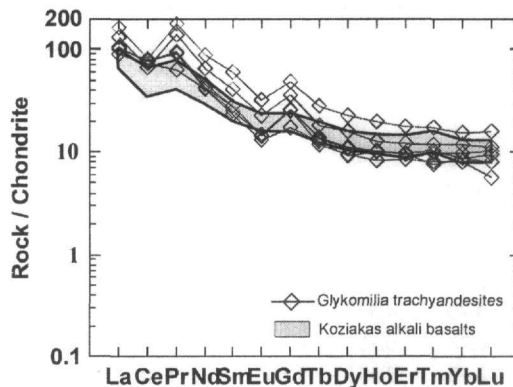


Figure 3. Chondrite-normalized REE diagram for the Glykomilia trachyandesites and Koziakas alkali basalts (normalized values after Nakamura et al., 1974).

In the diagram Th/Yb vs Ta/Yb (modified from Menzies and Kyle, 1990, Fig.4), the analyzed samples of Glykomilia trachyandesites plot at high Th/Yb values, in the field of rocks affected by crustal recycling or contamination, close to the Triassic volcanic rocks of Argolis and Othrys (Capedri et al., 1997). On the other hand, the Koziakas alkali basalts plot in the field of rocks with MORB and WPB affinities, which are unaffected by crust interaction, close to the alkali basalts of Avdella mélange (Pindos) and those of Evia (Capedri et al., 1997).

The alkali character of both studied volcanic rock-types is also consistent with the chondrite-normalized patterns (Fig.5). In this diagram, the patterns of alkali basalts are represented for comparison by an envelope, which outlines their maximum and minimum chondrite-normalized values. The patterns of both Glykomilia trachyandesites and Koziakas alkali basalts are subparallel with several enrichments particularly for LIL elements, whereas the HFSE are fractionated. Moreover, the trachyandesites are slightly richer in LIL elements than alkali basalts and display strong negative Nb, P, Ti and Y anomalies. We note that Nb depleted basalts with high Th values call for a descending slab activity (Dercourt, 1980; Rocci et al., 1980; Pe-Piper and Panagos, 1989). The similar and subparallel chondrite-normalized trace and REE patterns of both rock types, in combination with the distinct HREE-fractionation (see Fig.3) suggest a common mantle-source origin.

In the Hf/3-Th-Ta discrimination diagram (Wood, 1980; Fig.6) the alkali basalts plot in the field of Within Plate Basalts (WPB), whereas the Glykomilia trachyandesites plot in the field of Volcanic Arc Basalts (VAB), suggesting again that a subduction related environment has been involved in their genesis. The WPB geochemical affinities of the alkali basalts are also consistent with their REE and trace element patterns, which are similar to Ocean Island Basalts (OIB). Alkali basalt with OIB-like trace element assemblages is known from the Avdella mélange (Jones and Robertson, 1991), interpreted by Robertson et al. (1990) as seamounts in the Pindos ocean.

Our geochemical data could lead to the hypothesis that the trachyandesitic extrusive rocks of Glykomilia probably derived by partial melting of a LILE-enriched hydrous mantle, under spreading conditions (Pe-Piper, 1998; Turner and Hawkersworth, 1995). The small volume of these rocks is consistent with such an origin rather than by subduction. Furthermore, several authors believe that there is only little independent regional evidence for subduction in the Triassic Pindos basin (Hynes, 1974; Bebien et al., 1980; Duncan, 1987; Robertson et al., 1990). However, isotope and geochemical features suggest that hydration of the mantle may have taken place during an earlier Hercynian subduction (Pe-Piper 1998). This partial melting episode was probably induced by the uplift of an OIB-type

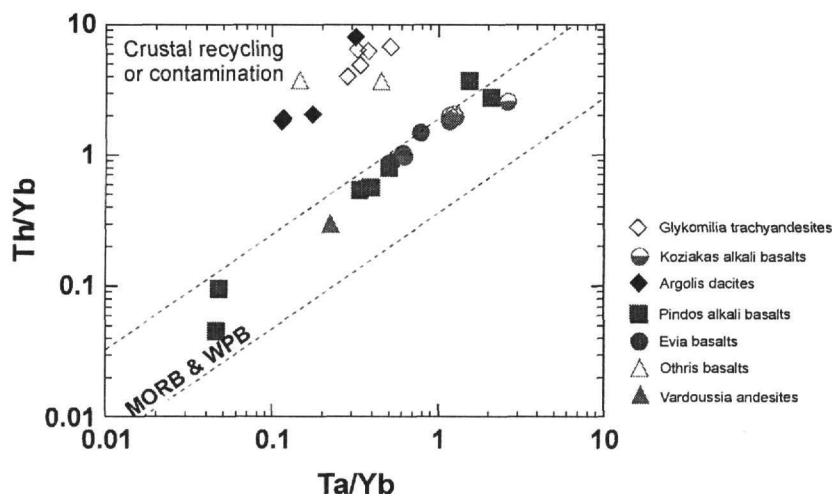


Figure 4. Th/Yb vs Ta/Yb (modified from Menzies and Kyle, 1990) for the Koziakas alkali basalts and Glykomilia trachyandesites, compared to other Triassic volcanic rocks from Greece and to Mid-Ocean ridge and Within plate volcanic rocks (diagonal dotted band of constant Th/ta ratio).

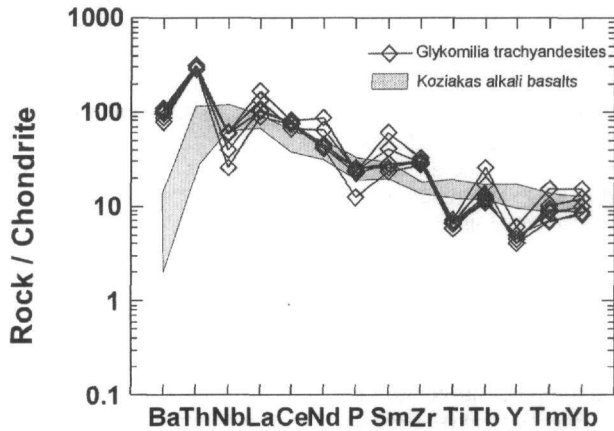


Figure 5. Chondrite-normalized trace-element diagram for the Glykomilia trachyandesites and Koziakas alkali basalts (normalized values after Thompson et al., 1984).

mantle plume, which subsequently gave rise to the WPB alkali basalts of the Koziakas ophiolite mélangé.

The close association of both the Glykomilia trachyandesites and the Koziakas alkali basalts with cherts lead to the hypothesis of eruption in a deep rift basin. Since the Glykomilia trachyandesites contain a "crustal" component, this occurred during a relatively short transitional period between the ending of continental rifting and the opening of the Pindos ocean. The presence of pillow textures and the absence of any "crustal" signature in alkali basalts support their extrusion onto the floor of an already evolved ocean basin, hence the alkali basalts evolved after the trachyandesites. In such a case, to explain the less differentiated nature of the Koziakas alkali basalts, we suggest that mixing of a primitive magma, produced from melting of a subducted lithosphere, with the already differentiated magma is required.

A contemporary formation of the Glykomilia trachyandesites and Koziakas alkali basalts is an also plausible hypothesis. In this case, the absence of the "crustal" component from the chemistry of the Koziakas alkali basalts could be explained if they had risen rapidly to the surface. On the other hand a relatively slower rise of Glykomilia trachyandesites, which characterized by extensive fractional crystallization, accompanied by "crustal" contamination.

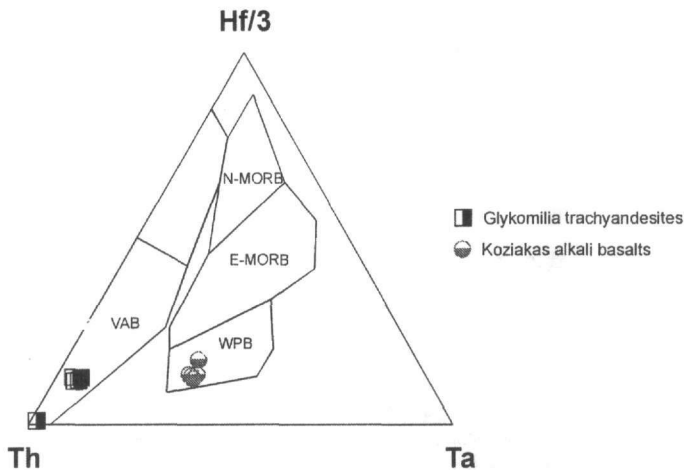


Figure 6. Hf/3-Th-Ta diagram (Wood, 1980) for the Glykomilia trachyandesites and Koziakas alkali basalts.



## 7 CONCLUSIONS

The Triassic trachyandesite found at the northern part of the Koziakas range and the alkali basalts, located into the ophiolitic mélange of the Koziakas ophiolite display similar alkaline geochemical characteristics. Although, the Glykomilia trachyandesites are more differentiated than the Koziakas alkali basalts and they have been affected by "crustal" contamination.

Both rock-types display similar, subparallel chondrite-normalized trace and rare earth element patterns, suggesting cogenetic origin. They illustrate LILE-enrichments and HFSE-depletions, resulted by their alkaline character. REE patterns are subparallel, enriched in LREE and show distinct HREE-fractionation, suggesting a common mantle-source origin for the trachyandesites and the alkali basalts. Furthermore, REE patterns and discrimination diagram plots reveal significant similarities to Triassic volcanic rocks from the Hellenides, suggesting also an island-arc signature for the Glykomilia trachyandesites and a WPB affinity for the alkali basalts.

The geochemical data presented here indicate that the trachyandesitic extrusive rocks of Glykomilia were probably derived by partial melting of a LILE-enriched hydrous mantle, under spreading conditions in a deep rift basin. This partial melting episode was probably induced by the uplift of an OIB-type mantle plume, which subsequently gave rise to the WPB alkali basalts of the Koziakas ophiolite mélange. The presence of pillow textures and the absence of any "crustal" signature in alkali basalts support their extrusion onto the floor of an already evolved ocean basin, hence the alkali basalts possibly evolved after the trachyandesites. In opposite, a contemporary formation of the Glykomilia trachyandesites and the Koziakas alkali basalts could be explained if the latter had risen rapidly to the surface.

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