

## ORIGIN OF THE HIGH-K TERTIARY MAGMATISM IN NORTHERN GREECE: IMPLICATIONS FOR MANTLE GEOCHEMISTRY AND GEOTECTONIC SETTING

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### Abstract

*Tertiary plutonic and volcanic rocks cropping out in the Rhodope Massif (N. Greece) are studied using existing and new geochemical and isotopic data. Most of these rocks belong to the post-collisional magmatism formed as part of the prolonged extensional tectonics of the Rhodope region in Late Cretaceous–Paleogene time. This magmatism is considered to be of mantle origin; however, the character of the mantle source is controversial. Rock bulk chemistry and compositional variations show magmas with calc-alkaline to high-K calc-alkaline and shoshonitic features associated with magmatism at convergent margins. Initial <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>143</sup>Nd/<sup>144</sup>Nd ratios, Pb isotopes and REE composition of the mafic rocks indicate mainly an enriched mantle source, even if some rocks indicate a depleted mantle source. Low- and High-K mafic members of these rocks coexist indicating a strongly heterogeneous mantle source. The High-K character of some of the mafic rocks is primarily strongly related to mantle enrichment by subduction-related components, rather than crustal contamination. The geochemical characteristics of the studied rocks (e.g. Ba/Th, Th/Yb, Ba/La, U/Th, Ce/Pb) indicate that primarily sediments and/or sediment melts, rather than fluid released by the subducted oceanic crust controlled the source enrichment under the Rhodope Massif.*

**Keywords:** Rhodope Massif, Mantle geochemistry, Geotectonic Setting, K-rich Magmatism.

### Περίληψη

*Τριτογενή πλουτωνικά και ηφαιστειακά πετρώματα που απαντώνται στη Μάζα της Ροδόπης (Β. Ελλάδα) μελετώνται χρησιμοποιώντας υπάρχοντα και νέα γεωχημικά και ισοτοπικά δεδομένα. Τα περισσότερα από τα πετρώματα αυτά ανήκουν στο μετά τη σύγκρουση μαγματισμό ο οποίος συνδέεται με την παρατεταμένη εφελκυστική τεκτονική στην περιοχή της Ροδόπης που χρονολογείται από το Κρητιδικό έως το Παλαιογενές. Ο μαγματισμός αυτός θεωρείται μανδρακής προελεύσεως όμως, ο χαρακτήρας της μανδρακής πηγής είναι αμφιλεγόμενος. Η χημική σύσταση των πετρωμάτων και οι συστασιακές μεταβολές δείχνουν μαγματισμό ασβεσταλκαλικού έως υψηλού-Καλίου και σωσσονιτικό χαρακτήρα που συνδέεται με συγκλίνοντα*

περιθώρια. Οι αρχικοί λόγοι  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  καθώς και τα ισότοπα Pb και η σύσταση σε Σπάνιες Γαίες των βασικών πετρωμάτων δείχνουν κυρίως εμπλουτισμένη μανδνακή πηγή αν και κάποια πετρώματα δείχνουν εκπτώχευμένη. Χαμηλού- και Υψηλού-Καλίου βασικά πετρώματα συνυπάρχουν, δείχνοντας μια έντονα ετερογενή μανδνακή πηγή. Ο υψηλού-Καλίου χαρακτήρας ορισμένων από τα βασικά πετρώματα είναι έντονα συνδεδεμένος με το μανδνακό εμπλουτισμό παρά με τη φλοιική μόλυνση. Τα γεωχημικά χαρακτηριστικά των πετρωμάτων αυτών (π.χ Ba/Th, Th/Yb, Ba/La, U/Th, Ce/Pb) δείχνουν ότι κυρίως ιζήματα και/ή τήγματα ιζημάτων παρά ρευστών που απελευθερώνονται από την υποβύθιση της ωκεάνιας πλάκας έλεγχαν τον εμπλουτισμό της πηγής κάτω από τη μάζα της Ροδόπης.  
**Λέξεις κλειδιά:** Μάζα Ροδόπης, Γεωχημεία Μανδύα, Γεωτεκτονικό Περιβάλλον, Υψηλού-Καλίου μαγματισμός.

## 1. Introduction

The Rhodope Massif (N. Greece) is defined as a key area for understanding the evolution of the Tethyan systems. Due to the complexity of the area many researchers have focused on its tectonic and magmatic evolution separately and some efforts have been made to combine petrology and tectonics. Various Tertiary plutonic and volcanic rocks crop out in the Rhodope Massif with most important occurrences those of Vrontou, Xanthi, Elatia, Maronia, Leptokarya-Treis Vryses-Chalasmata, Evros, Samothraki and Dipotama-Kalotyho (Figure 1). Different hypotheses have been suggested on the nature of the source and the crustal contamination controlling their composition. A great deal of research has been made regarding their geochemistry and evolution as well as their origin, and many geochemical data have been published (Del Moro et al., 1988; Eleftheriadis et al., 1989; Mavroudchiev et al., 1992; Jones et al., 1992; Pe-Piper et al., 1998; Christofides et al., 1998, 2002, 2011; Soldatos et al., 1998, 2008; Papadopoulou et al., 2004; Vlahou et al., 2006). The Tertiary magmatism of Rhodopes is considered as the result of crust-mantle interaction; however the nature of the mantle component is controversial. In order to address the nature of the mantle source, the role of crustal contamination and the process of their formation during the Tertiary tectonic events in Rhodope Massif the basic members of the magmatic rocks, which are considered crucial for the nature of their source, are studied. In detail, the trace element geochemistry and their isotopic characteristics are examined.

## 2. Geological Setting

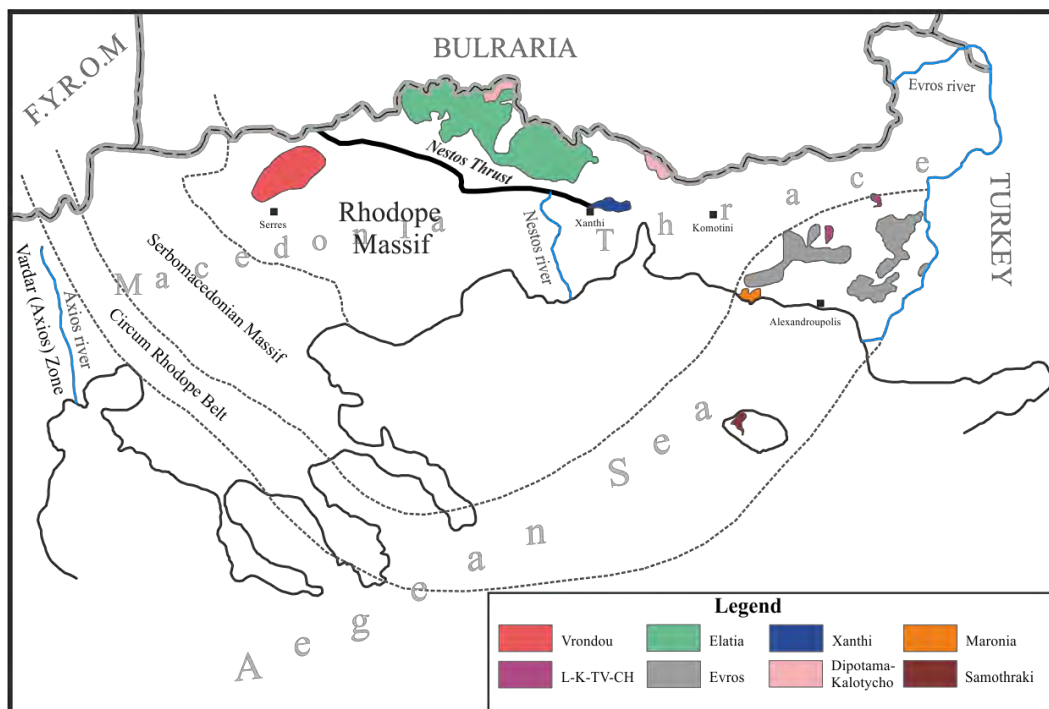
### 2.1 The Rhodope Massif

The Rhodope Massif (RM) is a polymetamorphic terrain extending along the Greek-Bulgarian border and covers part of the north-eastern Macedonia and western Thrace in Greece and south-eastern Bulgaria (Figure 1) as well as a small part of north-western Turkey. It is located in the frontal part of the Eurasian continental margin. It was assumed to have been formed from the closure of one subduction-exhumation cycle, the closure of the Paleo-Tethys ocean. It comprises mostly continental rocks with intercalations of oceanic material and represents the northernmost part of a southwest vergent Alpine nappe stack that developed during convergence between Africa and Europe from Jurassic to Neogene times (Papanikolaou and Panagopoulos, 1981; Burg et al., 1996; Ricou et al., 1998; Barr et al. 1999).

The northern border of the RM is defined by the west-northwestern-striking Maritsa fault in Bulgaria, which is composed of a series of subparallel, mainly dextral strike-slip faults (Burg et al. 1996, Georgiev et al., 2009). To the west the top-to-the-SW Tertiary Strymon detachment (Dinter and Royden, 1993; Sokoutis et al. 1993; Dinter et al. 1995; Lips et al. 2000) separates the RM from the Serbomacedonian Massif. To the east, the RM is structurally overlain by the Circum

Rhodore Belt (Kaufmann et al., 1976; Kockel et al., 1977; Meinhold et al., 2010), comprising greenschist-facies rocks and ophiolites.

The subdivision of RM into different units is a subject of debates by many workers (e.g., Papanikolaou and Panagopoulos 1981; Mposkos 1989; Kiliias and Mountrakis, 1990; Dinter et al., 1995; Burg et al. 1996; Krohe and Mposkos, 2002; Bonev et al., 2006; Georgiev et al., 2010; Turpaud, 2006; Bonev and Stampfli, 2008; Liati et al., 2011). Some schemes are based on structural criteria (e.g. Burg et al., 1996) other on metamorphic facies distinction (e.g. Krohe and Mposkos, 2002) and lately on geochronological data (Turpaud, 2006; Turpaud and Reischmann, 2010). A commonly used division for the Greek part of RM (central and western), based both on geological and petrological criteria, is the one proposed by Papanikolaou and Panagopoulos (1981), with an upper tectonic unit (UTU, also known as Sidironero unit) and a lower tectonic unit (LTU, also known as Pangaeo unit), separated by a SSE–NNW striking, northeast-dipping, thrust fault zone (Nestos thrust).



**Figure 1 – Schematic map of Northern Greece with the locations of the studied rocks.**

## 2.2 Tertiary Magmatic Activity

The extensional deformation of RM resulted in strong crustal thinning which started in Eocene (Kiliias et al, 1999; Burchfiel et al., 2003; Brun and Sokutis, 2007) or earlier in Early Paleocene (Bonev et al, 2006). A strong crustal thinning in back-arc areas is usually associated with magmatism. Post – collisional magmatism of Paleogene to Neogene age (plutonic and volcanic, Figure 1) variable in composition, space, and time dominates the RM (Koukouvelas & Pe-Piper, 1991; Dinter et al., 1995; Burg et al., 1996; Kiliias & Mountrakis, 1998; Christophides et al., 2001, 2004; Marchev et al., 2005; Bonev et al., 2006). Similar magmatic activity exists also in the continuation of RM in north-western Turkey (Bonev et al., 2007 and references therein). This magmatism is associated probably with the subduction of Pindos ocean; however, the remnant of the subducted slab of the Eastern margin of the opened, until the Tertiary time, Vardar-Axios ocean could also be the driving mechanism for the Tertiary magmatic activity in the Rhodope province or Vardar oceanic lithospheres (see Perugini et al., 2004; Kiliias et al., 2011).

The presence of fault-controlled extensional basins with intrusive and extrusive magmatism dominated the RM. Volcanic rocks are found north of Xanthi in the Dipotama-Kalotycho are, in western Thrace in the extensive area of Alexandroupolis the Evros volcanic rocks (EVR) and in the island of Samothraki (Figure 1). The **Dipotama-Kalotycho** Oligocene volcanic rocks cut across the crystalline basement of the RM and are structurally associated with the formation of sedimentary (extensional) basins and consist mainly of intermediate to basic rocks apart from the Dipotama area where only felsic rocks occur (Eleftheriadis, 1995). The **EVR** are in close association with fault-controlled sedimentary basins. Three volcanic areas, namely Loutros-Feres-Dadia, Kirki-Esimi and Mesti-Petrota, after the corresponding basins, are distinguished. Their composition ranges from basaltic andesite to rhyolite through andesite, trachyandesite, trachydacite and dacite (Christofides et al, 2002). It is to note that, since so far isotopic data are not available for the EVR, these rocks are not included in the present study. The **Samothraki volcanic rocks** are overlying an Eocene clastic neritic sequence. They are distinguished in three main groups based on their field occurrence and geochronology: the “old” group comprising basalts to latites, the “intermediate” group of andesites to latites and the “young” group of latites and rhyolites (Vlahou et al., 2006).

Many plutonic rocks of post-collisional origin are also found in the RM, apart from the **Elatia pluton** that is considered to be of subduction tectonic environment (Soldatos et al., 2008). It constitutes the main part of the Elatia-Skaloti-Paranesti granitic complex. Its main lithology is a (hornblende)-biotite granodiorite with a marginal porphyritic phase. The eastern part of the pluton is occupied by a two-mica granite which intrudes the granodiorite. The **Maronia pluton** northwards and westwards intrudes marbles of the metasedimentary series of the Makri unit causing a rather wide zone of contact metamorphism (skarn) (Doryphoros, 1990). Eastwards it intrudes a metamorphic sequence of phyllites, greenschists and gneisses of the overlying metavolcanosedimentary series of the same unit causing intense thermal metamorphism to the surrounding rocks (hornfels), while southwards the pluton itself is intruded by a small body of porphyritic micro-granite. Three main rock types have been distinguished: a) the basic group, with gabbros b) the intermediate group, with monzogranite to quartz-monzogranite and c) the felsic group, with granite in the form of dykes (Papadopoulou et al., 2004). The **Xanthi** pluton is in magmatic contact with Pangaion marbles to the west and gneisses and marbles of Sidironeron Unit. There is a contact metamorphic aureole typically a few hundred meters wide (Christofides, 1977; Liati, 1986). To the east the pluton cuts Eocene-Oligocene sedimentary rocks (dominantly flysch) which are intruded by andesitic dykes.

### 3. Analytical Methods

Some major elements used in the present study were taken from previous authors (Eleftheriadis, 1995; Christofides et al, 2002; Papadopoulou et al., 2004; Vlahou et al., 2006; Soldatos et al., 2008; Christofides et al. 2011) as well as the isotopic composition of Sr and Nd apart from the Xanthi and Vrontou plutons. The rest of the samples were analysed for major elements by X-ray fluorescence (XRF) in Saint Mary’s Univeristy, Halifax, Nova Scotia, Canada, and the Acme Analytical Laboratories (Vancouver) Ltd, Canada. All trace elements and REE analyses were performed on a laser ablation quadrupole inductively coupled plasma mass spectrometry (LA ICP-MS) in the Department of Earth Sciences, University of Perugia, Italy and on an quadrupole inductively coupled plasma mass spectrometry (ICP-MS) in the Acme Analytical Laboratories (Vancouver) Ltd, Canada. Additional analyses of some transitional elements already analyzed by ICP-MS, were determined by X-ray fluorescence (XRF) at Saint Mary’s Univeristy, Halifax, Nova Scotia, Canada. The isotopic Sr and Nd content from Xanthi and Vrontou samples were determined in the Department of Lithospheric Research, University of Vienna, Austria.

## **4. Geochemical Characteristics**

### **4.1 Major Elements**

Most samples both plutonic (Figure 2a) and volcanic (Figure 2b) belong to the calc-alkaline, high-K and shoshonitic series. All rocks demonstrate a wide range on SiO<sub>2</sub> content. The Elatia pluton consists mainly from felsic rocks and so far was considered to be of crustal origin. During the present work several mafic microgranular enclaves of basic composition were found on the northern part and analysed. This redefines the aspect of a crustal origin for the Elatia pluton and in the present paper is considered as a mantle derived rock.

### **4.2 Trace Elements**

Geochemical characteristics for representative mafic rocks are illustrated for each area in primitive mantle normalized multi-element diagrams (Figure 3). Most of the rocks, show similar patterns with LILE enrichment and HFSE depletion. Few basic rocks indicate LILE depletion which is not accompanied by HFSE enrichment. One sample from Samothraki and one from Vrontou show relative Nb and Ta enrichment. In Figure 4 trace elements diagrams are used as indicators of fluid or sediment component enrichment (a and b) of the mantle wedge and the degree of the source enrichment (c).

### **4.3 Rare Earth Elements (REE)**

The REE chondrite normalized patterns of the rocks are illustrated in the Figure 5. All rocks are enriched in LREE and slightly depleted in HREE. One sample of Samothraki exhibits parallel to Chondrite pattern showing a strongly depleted mantle source. Most samples exhibit negative Eu anomaly and some samples no Eu anomaly. Eu anomaly can be produced by plagioclase fractionation, residual plagioclase in the source or source contamination by slab-derived fluids and sediments (Ellam & Hawkesworth, 1988). Since most samples have high Al content it means that they have not undergone significant plagioclase fractionation but contamination from the Rhodope metamorphic lithologies or source contamination from the subducted crust.

### **4.4 Isotopic Data**

In Figure 6 the <sup>143</sup>Nd/<sup>144</sup>Nd vs <sup>87</sup>Sr/<sup>86</sup>Sr available data are illustrated. There is a wide range on both Nd and Sr isotopes for each area which implies the different degrees of contamination. Most samples are plotted between EM-I (Enriched Mantle I) and EM-II (Enriched Mantle II) mantle reservoirs supporting the enriched mantle source of these rocks. There are samples that demonstrate a more depleted component both for Nd and Sr isotopes especially samples from Xanthi, Samothraki and Elatia and the trend of most samples is towards DMM reservoir rather than continental crust.

## **5. Discussion and Conclusions**

The Rhodope magmatic rocks are undoubtedly of orogenic origin as already stated by many previous workers (see 2.2). A subduction mechanism proposed for the Tertiary magmatism of Rhodope which persisted for many million years. Due to the variations on the Rhodope magmatism many more complicated subduction models have been proposed (see Marchev et al., 2004). Moreover asthenospheric contribution is confirmed in the Bulgarian part of Rhodope. Rollback and slab break off is one of them and was suggested for the magmatism in the Aegean region. It leads to the heating of the lithospheric mantle by upwelling of the asthenosphere and melting of its enriched layers. Different degrees of partial melting produce magmas ranging from alkaline to ultrapotassic, whereas slightly higher degrees of melting produce calc-alkaline melts. Another model is delamination of the thickened crust after the continental collision proposed by

Yanef et al. (1998). It differs from the slab break off model cause it predicts rapid intrusion of the asthenosphere in the place of the delaminated mantle and eclogitized lower crust resulting in uplift

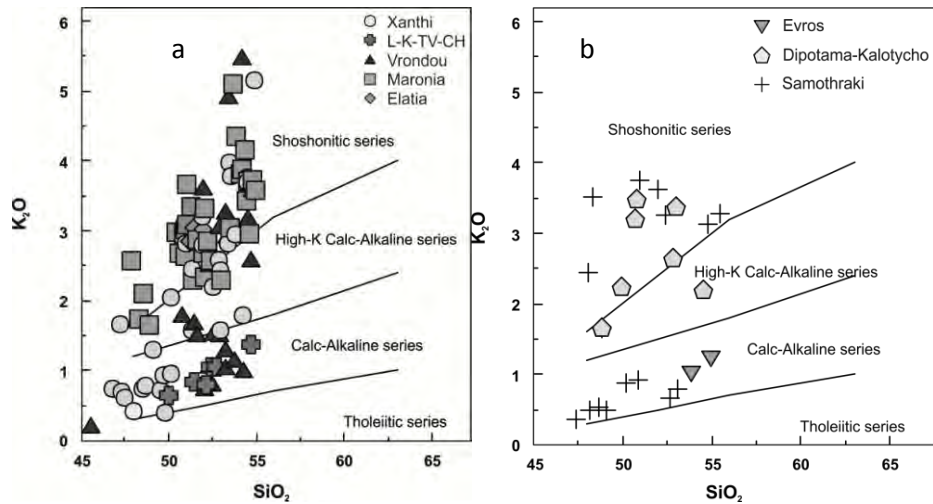


Figure 2 - SiO<sub>2</sub> vs K<sub>2</sub>O of the plutonic rocks (a) and volcanic rocks (b) after Peccerillo & Taylor 1976.

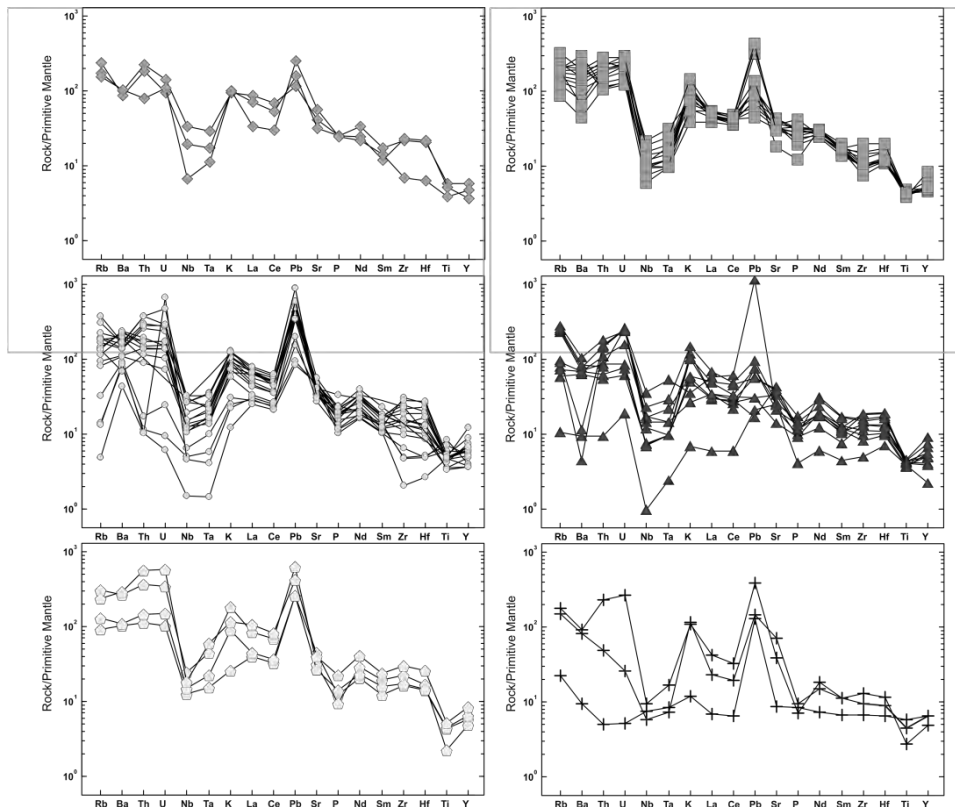
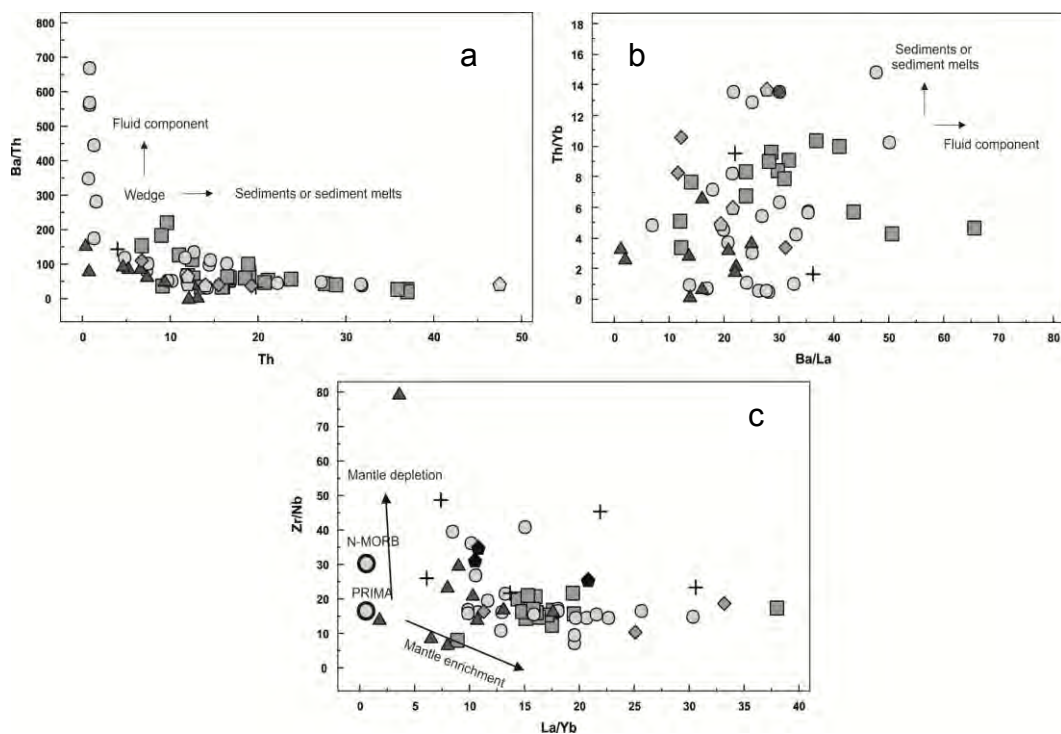


Figure 3 - Primitive mantle normalized multi-element diagrams. Normalization values after Sun & McDonough (1989). Symbols as in Figure 2.



**Figure 4 - a) Ba/Th vs Th as indicator of fluid or sediment component (Elliot et al., 1997) b) Th/Yb vs Ba/La as indicator of fluid or sediment component (Hawkesworth et al., 1997) c) Zr/Nb vs La/Yb for source enrichment (Münker, 2000). Symbols as in Figure 2.**

and extensional collapse. Convective removal is another subduction model which predicts convective thinning of the unstable thickened lithospheric mantle and may result in removal of the whole mantle lithosphere and its replacement by hot asthenosphere. This will cause fast uplift of the overlying crust. According to Marchev et al. (2004) the above models have many shortcomings and are not able to describe the Rhodope magmatism. The same authors propose a form of convective thinning of the lithosphere and of mantle diapirism due to asthenospheric origin of basalts they analyzed. So far, due to the lack of asthenospheric derived rocks in the Greek part of the Rhodope Massif, the above theory seems to interpret the Tertiary Rhodopian magmatism better than the previous. A more satisfactory explanation needs to be proposed and is under study for the Greek part of Rhodope.

Regarding the available geochemical data, an enriched and depleted mantle source existed simultaneously and generated the magmatic rocks of Rhodope. A 'leopard skin' mantle wedge during the Tertiary, which was able to produce a wide range of mafic magmas has been proposed from Perugini et al. (2004) to explain the heterogeneous mantle under RM. The same authors proposed the influence of the uprising asthenospheric mantle since the high  $K_2O$  and the high LILE abundances are not in agreement with the relatively low Sr and high Nd isotopic values. Nevertheless, satisfactory data to support the above proposal are missing.

The enrichment of the mantle wedge above the subducted oceanic crust was caused from sediments or sediment melts derived from the subducted ocean. The MORB-like patterns of some dykes from Samothraki reflects strong mantle depletion. The no-negative Nb-Ta anomaly of one sample from Samothraki may imply asthenospheric contribution. The present study is in progress and more geochemical and isotopic data are to be presented in order to give satisfactory explanations on the nature of the Rhodopian magmatism and the processes that took place.

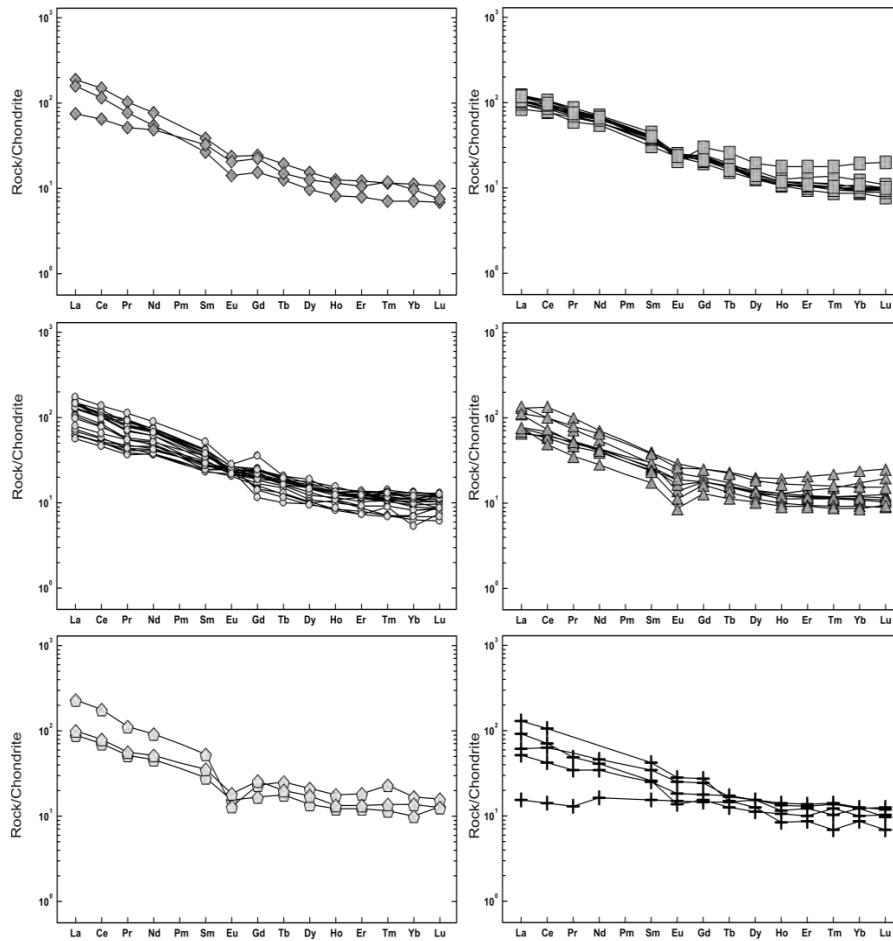


Figure 5 - Chondrite normalized multi-element diagrams. Normalization values after Boynton (1984). Symbols as in Figure 2.

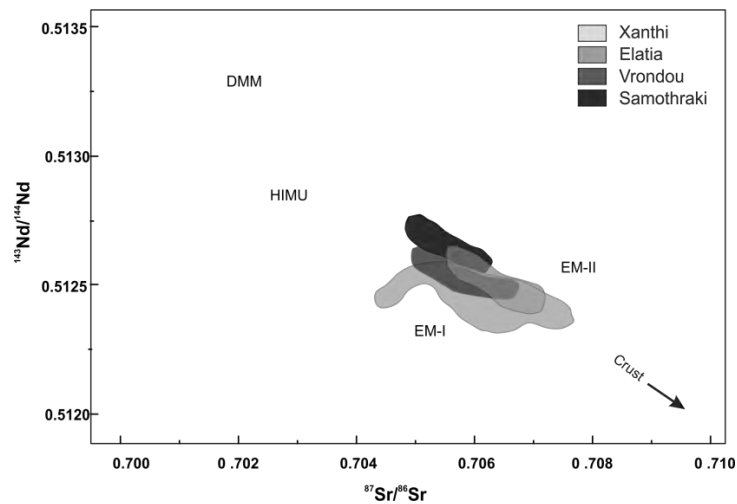


Figure 6 -  $^{143}\text{Nd}/^{144}\text{Nd}$  vs  $^{87}\text{Sr}/^{86}\text{Sr}$  with some mantle reservoirs illustrated. Symbols as in Figure 2.



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