

## Pre-Tertiary A-Type magmatism in the Serbomacedonian massif (N. Greece): Kerkini granitic complex

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### ABSTRACT

The Kerkini granitic complex occurs in Mt. Kerkini intruding the NW Vertiskos unit of the Serbomacedonian massif in northern Greece. It consists of three bodies, the Muries granite (MUR) which is the largest intrusion, an apophyses of it to the south known as the Miriofito granite (MIR), and the Kastanusa (KAS) granodiorite to the east. The complex is intensively deformed and weathered. The main rock-type is two-mica granite with subordinate biotite and white mica granite. The rocks are medium- to coarse-grained, leucocratic to mesocratic, with allotriomorphic granular to hypidiomorphic inequigranular textures.

Feldspars are represented by albite and perthitic microcline. Biotite is late in the crystallization sequence (interstitial) and its composition is mostly close to annite end-member. White mica is phengite. Minimum pressure calculated from the phengite barometer ranges from 4 to 10 kbar. Accessory fluorite is also present.

The rocks have features characteristic for A-type granites. They are peraluminous ( $A/CNK=1.0-1.3$ ), depleted in MgO and CaO, enriched in total alkalis and have high FeOt/MgO ratios. They are enriched in Zr, Nb, Y, Ga and REE, and have strongly negative Eu anomaly. They plot in the A-type granite fields of various discriminant diagrams and their chemistry suggests a WPG tectonic environment. The KAS granodiorite shows a few differences in chemical composition compared with the MUR and MIR granites. Sr initial ratio for one MUR sample based on 130 Ma is 0.7275.

K-Ar dating on micas yielded a Lower Cretaceous age for the Kerkini granitic complex (MUR granite). Biotite separates gave ages of  $130\pm 3$  Ma and  $131\pm 3$  Ma and muscovite an age of  $133\pm 3$  Ma. These ages are younger than the ages of the rest of the "Jurassic" granitic rocks in Serbomacedonian massif and Axios (Vardar) zone and are considered to reflect an unroofing or retrograde metamorphic event. The genesis of the Kerkini granitic complex is probably related with a Late Jurassic magmatic event.

The most probable genetic model for the origin of the MUR and MIR granites is fluid-absent melting of a biotite-rich tonalitic source at 6 - 10 kbar and 950 - 975 °C, leaving behind a granulitic residue dominated by orthopyroxene, quartz and plagioclase.

### ΠΕΡΙΛΗΨΗ

Το γρανιτικό σύμπλεγμα της Κερκίνης βρίσκεται στο όρος Κερκίνη διεισδύοντας τη σειρά του ΝΔ Βερτίσκου της Σερβομακεδονικής μάζας στη Β. Ελλάδα. Συνίσταται από τρία σώματα το μεγαλύτερο από τα οποία είναι ο γρανίτης των Μουριών (MUR). Μια απόφυσή του προς νότο αποτελεί το

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γρανίτη του Μυριόφυτου (MIR) ενώ μια άλλη διείδυση στα ανατολικά είναι γνωστή ως γρανίτης της Καστανούσας (KAS). Το σύμπλεγμα είναι έντονα παραμορφωμένο και αρκετά αλλοιωμένο. Ο κύριος πετρογραφικός τύπος είναι ο διμαρμαρυγιακός γρανίτης ενώ απαντούν τοπικά ο βιοτιτικός και ο μοσχοβιτικός γρανίτης. Τα πετρώματα είναι μεσόκοκκα έως χονδρόκοκκα, λευκοκρατικά έως μεσοκρατικά, με αλλοτριόμορφο κοκκώδη και υπιδιόμορφο ανισότροπο ιστό.

Οι άστριοι αντιπροσωπεύονται από αλβίτη και νεφθιτικό μικροκλινή. Ο βιοτίτης κρυσταλλώνεται στα διάκενα των αστρών και του χαλαζία μετά από αυτούς και η σύστασή του, με μια εξαιρεση, πλησιάζει τη σύσταση του αννίτη. Ο λευκός μαρμαρυγιας είναι φενγκίτης και με το γεωβαρόμετρό του υπολογίσθηκαν ελάχιστες πιέσεις που κυμαίνονται από 4 μέχρι 10 kbar. Χαρακτηριστικό του συμπλέγματος είναι η παρουσία φθορίτη ως επουσιώδους ορυκτού.

Τα πετρώματα του συμπλέγματος παρουσιάζουν γνωρίσματα χαρακτηριστικά των Α-τύπου γρανιτών. Είναι υπεραργιλικά ( $A/CNK=1.0-1.3$ ), πτωχά σε  $MgO$  και  $CaO$ , εμπλουτισμένα σε ολικά αλκάλια, και έχουν υψηλές αναλογίες  $FeO_t/MgO$ . Είναι εμπλουτισμένα σε  $Zr$ ,  $Nb$ ,  $Y$ ,  $Ga$  και  $REE$ , και παρουσιάζουν έντονη αρνητική ανωμαλία  $Eu$ . Προβάλλονται στο πεδίο των Α-τύπου γρανιτών σε διάφορα διακριτικά διαγράμματα ενώ η γεωχημεία τους υποστηρίζει γεωτεκτονικό περιβάλλον ενδοπλακικών (WPG) γρανιτών. Ο γρανοδιόριτης της Καστανούσας παρουσιάζει μερικές διαφορές ως προς τη χημική του σύσταση συγκρινόμενος με τους γρανίτες των Μουριών και του Μυριόφυτου. Η αρχική αναλογία  $Sr$ , βασισμένη στην ηλικία των 130 Ma, για ένα δείγμα από το γρανίτη των Μουριών είναι 0.7275.

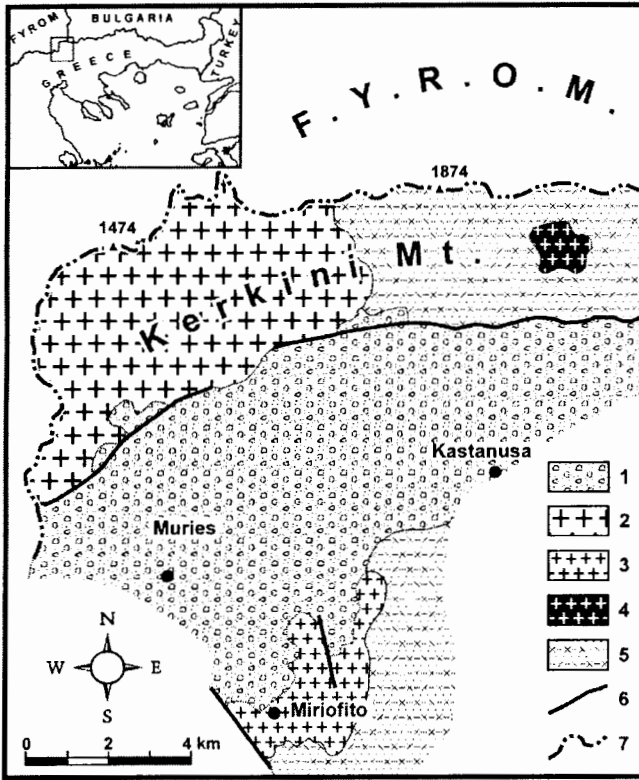
Γεωχρονολογήσεις K-Ar σε μαρμαρυγίες από τρία δείγματα του γρανίτη των Μουριών έδωσαν ηλικία Κάτω Κρητιδικού. Συγκεκριμένα οι βιοτίτες έδωσαν ηλικίες  $130\pm 3$  Ma και  $131\pm 3$  Ma ενώ ο μοσχοβίτης  $133\pm 3$  Ma. Οι ηλικίες αυτές είναι νεότερες από τις ηλικίες των άλλων "Ιουρασικών" γρανιτικών πετρωμάτων της Σερβομακεδονικής μάζας και της ζώνης του Αξιού και θεωρείται ότι αντιπροσωπεύουν ένα ανάδρομο μεταμορφικό γεγονός ή τεκτονική αποκάλυψη (unroofing) κατωκρητιδικής ηλικίας. Η γένεση του γρανιτικού συμπλέγματος της Κερκίνης συνδέεται πιθανότατα με τον ανωιουρασικής ηλικίας μαγματισμό που έδωσε αρκετούς γρανίτες στην περιοχή.

## INTRODUCTION

Two fundamentally different types of granitic rocks were recognised by Chappell & White (1974) and White & Chappell (1977) who designated those with characteristics indicating derivation from meta-sedimentary protoliths as S-type and those with characteristics indicating derivation from meta-igneous or igneous protoliths as I-type. White (1979) defined a third granitoid type (M-type) which was presumably directly derived from the melting of subducted oceanic crust or the overlying mantle. Another distinctive group of granites has since been designated "A-type" by Loiselle & Wones (1979) who used the term to emphasize the anorogenic tectonic setting and the relative alkaline composition as well as the supposedly anhydrous character of the magmas. These authors (Loiselle & Wones pers. comm. 1980, 1984, from

Clemens et al., 1986) also emphasized that unlike the S-, I- and M-type, A-type classification does not imply a specific source or mode of origin. However, since then various proposals have been made concerning source and mode of origin of A-type granites (Clemens et al., 1986; Whalen et al., 1987; Eby, 1990, 1992; Creaser et al., 1991, Skjerlie & Johnston, 1993 and Landenberger & Collins, 1996).

In the Serbomacedonian massif (SMM) in northern Greece numerous felsic plutonic and volcanic rocks of Jurassic to Tertiary age occur. The presence of granitoids in such a complex geotectonic unit as is the SMM is of particular importance since, through their geochemistry and tectonics, they can potentially constrain the timing of the main tectonic events in it. Some of the young (Tertiary) granitoids (Sithonia, Ouranoupolis; Christofides et al. (1986), D' Amico et al. (1990),



**Figure 1.** Geological map of the Kerkini granitic complex. 1:Alluvial; 2:Muries (MUR) granite; 3:Miriofito (MIR) granite; 4: Kastanusa (KAS) granodiorite; 5:Metamorphic basement; 6:Fault; 7:State boundary.

rocks. K-Ar age data on biotite and white mica are presented along with petrological and geochemical data to add constraints on the SMM magmatism.

### GEOLOGICAL SETTING

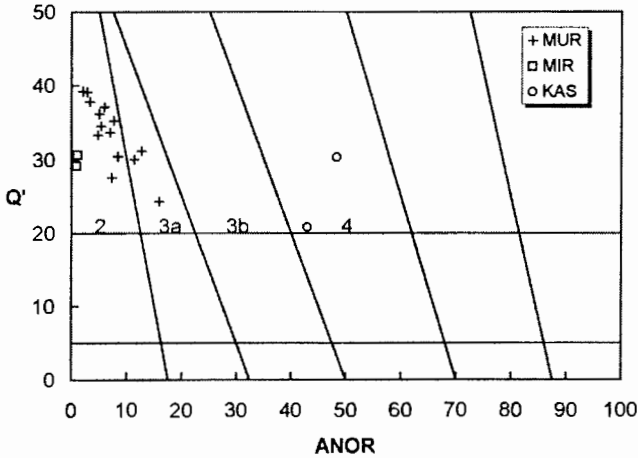
The SMM is a complex geotectonic unit which underwent major mid-Mesozoic metamorphic, magmatic and deformational events (Dixon & Dimitriadis, 1984; Sakellariou, 1989) followed by Eocene and Oligocene plutonism (D'Amico et al., 1990; Frei, 1992). It extends as a long and narrow zone in a SSE direction from near Belgrade

De Wet et al. (1989), have been studied in some detail, contributing thus in the establishment of the Tertiary geological history in this area. Among the older, however, intrusions, known as the "Jurassic" granitoids (Kockel et al., 1977), only a few have been investigated. Christofides et al. (1990) and Soldatos et al. (1993) gave geochemical data and presented major and trace element models for the Late Jurassic Fanos granite evolution. De Wet et al. (1989) and De Wet (1989) gave significant isotopic data on the Late Jurassic to Early Cretaceous Arnea granite. Monopigadon granite which is also of Late Jurassic age was investigated by Ricou (1965) and Michard et al. (1998). The rest of the SMM "Jurassic" granitoids, e.g. Kerkini granitic complex, have been given little attention.

In this work we investigate the Kerkini granitic complex which mostly comprises A-type granitic

in Serbia to the Chalkidiki peninsula in Greece. Based on lithologies and grade of metamorphism it is divided into two units namely the Kerdyllia unit, a small area in NE Chalkidiki comprising gneisses, amphibolites and marbles metamorphosed under upper amphibolite facies conditions and the Vertiskos unit to the west which is in a tectonic contact with the upper marble horizon of the Kerdyllia unit and comprises various types of gneisses, and amphibolites, metamorphosed under lower amphibolite facies conditions.

The Kerkini granitic complex intrudes the NW Vertiskos unit north of Muries village in Mt. Kerkini straddling the Greece - F.Y.R.O.M. border (Fig. 1). It comprises a large intrusion namely the Muries granite (MUR), and the Kastanusa (KAS) granodiorite which consists of a small intrusion to the east. An apophyses of the Muries granite to the south, known as the Miriofito granite (MIR)



**Figure 2.** Classification of the analysed samples of the Kerkini granitic complex on the Q-ANOR diagram of Streckeisen & Le Maitre (1979). 2:alkali granite, 3:granite, 4:granodiorite.

(Sidiropoulos, 1991), is separated from the main granitic body by the Doirani-Kerkini basin. The country rocks comprise two-mica and amphibole gneisses, schists and amphibolites. Small outcrops of meta-ultrabasic rocks and marbles are also present. The southern and the western contacts of the MUR granite are strongly deformed. Mylonitic fabrics in the granite, especially at the western contact, are well-developed. No contact metamorphism has been observed. Along the road leading to the Border Control Army Station, the MUR granite alternates with muscovite schists similar to those found along the southwest margin of the granite.

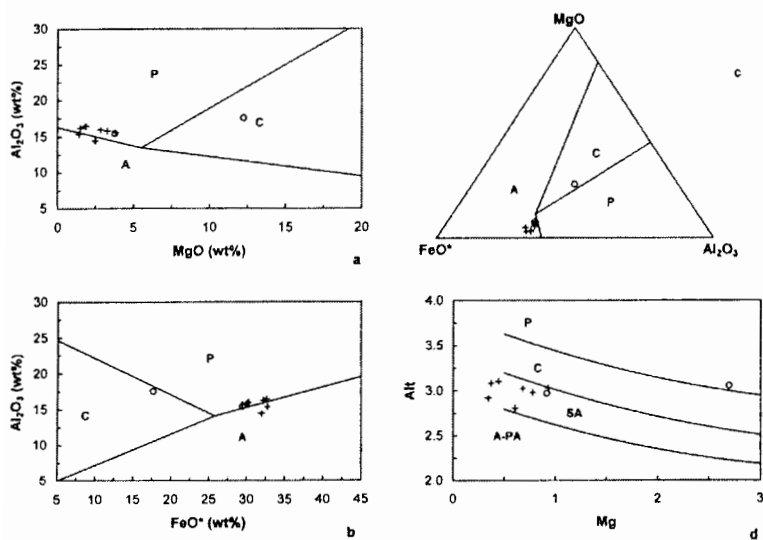
### PETROGRAPHY

The Q-ANOR diagram (Fig. 2) of Streckeisen & Le Maitre (1979) has been used for the classification of the rocks studied. MUR and MIR rocks are classified as alkali granite to granite whereas KAS rocks classify as granodiorite.

The Kerkini granitic complex is intensively deformed and weathered. The less deformed is the MIR granite which, however, is hydrothermally altered. Fresh samples can only be collected from road sections and torrent tracks. The less weathered is the KAS granodiorite which is also the most biotite rich. The main rock-type is two-mica granite with subordinate biotite and muscovite granite. The rocks are medium- to coarse-grained,

leucocratic to mesocratic, although fine-grained types are also present with allotriomorphic granular to hypidiomorphic inequigranular textures. Subhedral to euhedral perthitic K-feldspar phenocrysts, set in a fine- to medium-grained quartz-feldspar-mica matrix occur in the latter texture. Graphic intergrowths are often developed.

The main mineral constituents are quartz, K-feldspar, plagioclase, biotite and white mica. Accessories include opaque, mostly sulfides, zircon, allanite, apatite, fluorite and titanite. Chlorite, epidote and sericite occur as secondary minerals. Quartz occurs in large subhedral crystals although it more commonly is found as fine-grained anhedral grains. It is sometimes recrystallized and forms symplectites with micas. K-feldspar ( $Or_{94-98}$ ), mostly microcline, occurs as perthitic to microperthitic anhedral crystals and as subhedral to euhedral perthitic phenocrysts. Plagioclase is mostly albite (core:  $Ab_{88-99}$ , rim:  $Ab_{87-99}$ ), occurring in subhedral to anhedral crystals, often poorly zoned. Alteration to sericite is not uncommon. Biotite is close to annite end-member except one analysis in KAS (Tab. 1). It is late in the crystallization sequence occurring as interstitial grains between feldspars and quartz. Biotite is frequently altered to chlorite and sometimes to epidote and Fe-Ti oxides. On the discriminant diagrams of Abdel-Rahman (1994) (Fig. 3a-c) biotites from MUR plot either in the alkaline field or straddle the peraluminous-alkaline fields. The same behaviour is shown by MP-13 of KAS group while MP-12 of the same group plots in the calc-alkaline field. On the Nachit et al. (1985)  $Al_1$  - Mg diagram the MIR and MP-13 samples plot in the sub-alkaline field (Fig. 3d) while MP-12 falls in the peraluminous field. The Si content of



**Figure 3.** Plot of the biotites of the MUR and KAS rock-groups on the Abdel-Rahman (1994) (a, b, c) and on the Nachit et al. (1985) (d) discrimination diagrams. A: alkaline; C: calc-alkaline; P: peraluminous; S: sub-alkaline; A-PA: alkaline-peralkaline field. Symbols as in figure 2.

the white mica ranges from 6.4 to 6.7 (based on 22 O) and its celadonite component is 22.8 - 36.8 indicating that it is actually a phengite. Microscopically it has features (grain size comparable to other primary phases, subhedral form, not enclosed by other minerals) favouring a primary origin. However, its chemistry rules out such an origin; in terms of Ti, Na and Mg, its analysed grains mostly plot in the secondary muscovite field after Miller et al. (1981). Moreover its  $TiO_2$  content is <0.6% (Zen, 1988). If it is of primary origin and if we assume temperatures of 400°C and 500°C (presence of microcline) minimum pressure calculated for the phengite formation using the Massonne & Schreyer (1987) barometer ranges from 4 to 10 kbar. These pressures must be considered with caution due on the one hand to the potential of the phengite barometer (see Anderson, 1996) and on the other hand to the ambiguity of the origin of the white mica in the Kerkini rocks.

Microprobe analyses of the mineral constituents are given in table 1.

## GEOCHEMISTRY

Major and trace element analyses of 18 selected granitic samples were determined by XRF. Six of them were analysed for REE and some

trace elements by INAA. Chemical data of the analysed samples are presented in table 2. Major and trace element compositional variations are depicted in figures 4 and 5 respectively, while REE pattern and variation diagrams are shown in figure 6.

The  $SiO_2$  content of the MUR granite complex range from 70.4% to 75.8 wt%. All major elements decrease with increasing  $SiO_2$ .  $Na_2O+K_2O$  is high, ranging from 8.2 to 9.5 wt% while CaO is low <1.5 wt% and in most samples <0.7 wt%. Although  $(Na_2O+K_2O)/Al_2O_3$  is high, none of the rocks is peralkaline.  $FeO/MgO$  ratio ranges from 6.2 to 19.1. The trace elements are negatively correlated with  $SiO_2$  except Rb which is either constant or shows a slight increase. The rocks in general are enriched in Zr, Nb, Rb, Y, Th and U (Table 2). The REE patterns of all samples are similar and quite enriched relative to chondrite ( $La_{CN}=150-220$ ) but with slight LREE enrichment [ $(La/Lu)_{CN}=3-6$ ] which increases with  $SiO_2$ .  $\Sigma REE$  ranges from 214 to 315 ppm decreasing with  $SiO_2$ . The REE patterns show a large negative Eu anomaly ( $Eu/Eu^*=0.06-0.30$ ) which increases with increasing Sr contents.

Compared with the MUR granite the KAS granodiorite shows a few differences. The most no-

Sample Type	PLAGIOCLASE											K-FELDSPAR										
	MP-101	MP-102	MP-104	MP-106	MP-105	MP-23	MP-21	MP-108	MP-111	MP-12	MP-13	MP-101	MP-102	MP-104	MP-106	MP-105	MP-23	MP-21	MP-108	MP-111		
SiO <sub>2</sub>	64.96	66.39	68.02	66.45	68.98	68.31	68.51	67.02	67.42	68.63	67.25	65.40	64.89	64.54	65.50	64.71	65.77	65.26	65.11	66.11		
TiO <sub>2</sub>	0.13	0.02	0.00	0.00	0.00	0.00	0.05	0.04	0.06	0.00	0.00	0.09	0.00	0.03	0.00	0.00	0.00	0.07	0.00	0.00		
Al <sub>2</sub> O <sub>3</sub>	20.89	20.13	20.03	20.26	19.57	20.09	19.84	20.07	19.78	19.81	20.98	18.56	18.71	18.26	18.82	18.03	17.63	18.16	18.80	17.82		
FeO*	0.00	0.02	0.05	0.00	0.06	0.06	0.22	0.04	0.10	0.01	0.00	0.15	0.00	0.07	0.00	0.04	0.04	0.01	0.07	0.03		
CaO	1.60	0.75	0.62	1.18	0.42	1.48	0.65	0.62	0.07	0.73	2.22	0.00	0.00	0.01	0.00	0.01	0.05	0.03	0.00	0.00		
Na <sub>2</sub> O	11.72	12.16	11.87	11.80	11.15	9.50	11.08	12.19	12.48	10.86	9.63	0.60	0.53	0.52	0.80	0.58	0.40	0.38	0.55	0.26		
K <sub>2</sub> O	0.16	0.01	0.13	0.10	0.08	0.11	0.02	0.06	0.07	0.05	0.13	15.05	15.53	16.00	15.60	16.19	15.67	15.52	15.92	15.92		
Total	99.46	99.47	100.71	99.79	100.27	99.56	100.21	100.03	99.95	100.15	100.21	99.86	99.67	99.44	100.51	99.53	100.09	100.26	100.14	100.14		
Structural formulae on the basis of 8 O																						
Si	2.88	2.93	2.96	2.93	3.00	2.98	2.98	2.94	2.96	2.99	2.93	3.00	3.00	3.00	3.00	3.01	3.03	3.02	2.99	3.04		
Al	1.09	1.05	1.03	1.05	1.00	1.03	1.02	1.04	1.02	1.02	1.08	1.00	1.02	1.00	1.01	0.99	0.96	0.98	1.02	0.96		
Fe <sup>3+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Z	3.98	3.98	3.99	3.98	4.00	4.02	4.01	3.99	3.99	4.01	4.02	4.01	4.00	4.00	4.00	3.99	3.99	4.01	4.01	4.00		
Ca	0.08	0.04	0.03	0.06	0.02	0.07	0.03	0.03	0.00	0.03	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Na	1.01	1.04	1.00	1.01	0.94	0.80	0.93	1.04	1.06	0.92	0.81	0.05	0.05	0.05	0.05	0.04	0.03	0.05	0.02	0.02		
K	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.88	0.91	0.95	0.91	0.96	0.95	0.92	0.91	0.93		
X	1.09	1.08	1.04	1.07	0.96	0.88	0.96	1.07	1.07	0.95	0.92	0.94	0.96	1.00	0.96	1.01	0.99	0.95	0.96	0.96		
Or	0.83	0.03	0.68	0.50	0.44	0.72	0.72	0.30	0.38	0.31	0.78	94.27	95.07	95.21	94.48	94.68	96.12	96.31	94.92	97.54		
Ab	92.21	96.69	96.53	94.31	97.43	91.39	96.71	96.98	99.32	96.12	88.02	5.73	4.93	4.74	5.82	5.21	3.62	3.53	5.07	2.46		
An	6.96	3.28	2.79	5.19	2.13	7.89	3.15	2.72	0.29	3.57	11.19	0.00	0.00	0.00	0.00	0.11	0.27	0.17	0.01	0.00		
Structural formulae on the basis of 22 O																						
Si	5.65	5.60	5.54	5.59	5.58	5.63	5.62	5.32	5.32	5.50	6.41	6.54	6.55	6.46	6.45	6.54	6.57	6.52	6.46	6.73		
Al <sup>IV</sup>	2.35	2.40	2.46	2.41	2.42	2.37	2.53	2.38	2.68	1.50	1.59	1.46	1.45	1.54	1.27	1.54	1.80	1.80	1.80	1.80		
Z	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00		
Al <sup>VI</sup>	0.67	0.58	0.56	0.39	0.50	0.71	0.57	0.68	0.29	3.05	3.10	2.97	3.07	3.19	3.14	3.14	3.14	3.14	3.14	3.14		
Ti	0.23	0.26	0.30	0.30	0.34	0.23	0.31	0.20	0.46	0.04	0.03	0.06	0.03	0.04	0.08	0.08	0.08	0.08	0.08	0.08		
Fe <sup>3+</sup>	4.04	4.01	4.07	4.05	4.42	4.35	4.36	2.18	4.02	0.83	0.88	0.79	0.82	0.77	0.66	0.66	0.66	0.66	0.66	0.66		
Mn	0.08	0.07	0.07	0.05	0.06	0.00	0.04	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00		
Mg	0.93	0.78	0.68	0.61	0.34	0.37	0.44	2.69	0.92	0.29	0.22	0.36	0.21	0.16	0.20	0.20	0.20	0.20	0.20	0.20		
Y	5.96	5.69	5.68	5.74	5.67	5.65	5.73	5.76	5.73	4.21	4.24	4.18	4.15	4.16	4.07	4.07	4.07	4.07	4.07	4.07		
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Na	1.21	0.12	0.16	0.01	0.08	0.08	0.08	0.12	0.08	0.12	0.11	0.07	0.06	0.10	0.04	0.04	0.04	0.04	0.04	0.04		
K	0.08	1.81	1.78	1.92	1.85	1.82	1.72	1.71	1.89	1.83	1.82	1.93	1.97	1.85	1.80	1.84	1.84	1.84	1.84	1.84		
X	1.30	1.93	1.94	1.94	1.91	1.90	1.89	2.01	1.96	1.93	2.00	2.02	1.95	1.84	1.84	1.84	1.84	1.84	1.84	1.84		

**Table 1** Microprobe analyses and structural formulae of plagioclase, K-feldspar, biotite and white mica from the Kerkini granitic complex

table are the higher Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O contents and the significantly lower K<sub>2</sub>O content in the granodiorite. Its trace elements are also different particularly, V, Nb, Zr, Y, Rb, Ba and Sr. The difference in the last three elements is obvious in the  $\Phi\eta\phi\iota\alpha\kappa\eta$  Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας, Α.Π.Θ.

Rb-Sr-Ba diagram of Bouseilly & Sokkary (1975) where the MUR plots in the normal and strongly differentiated granite fields while the KAS falls in the field of granodiorite and quartz diorite (Fig. 7). The KAS REE pattern is similar to those of MUR in

FeO\* = total iron as ferrous

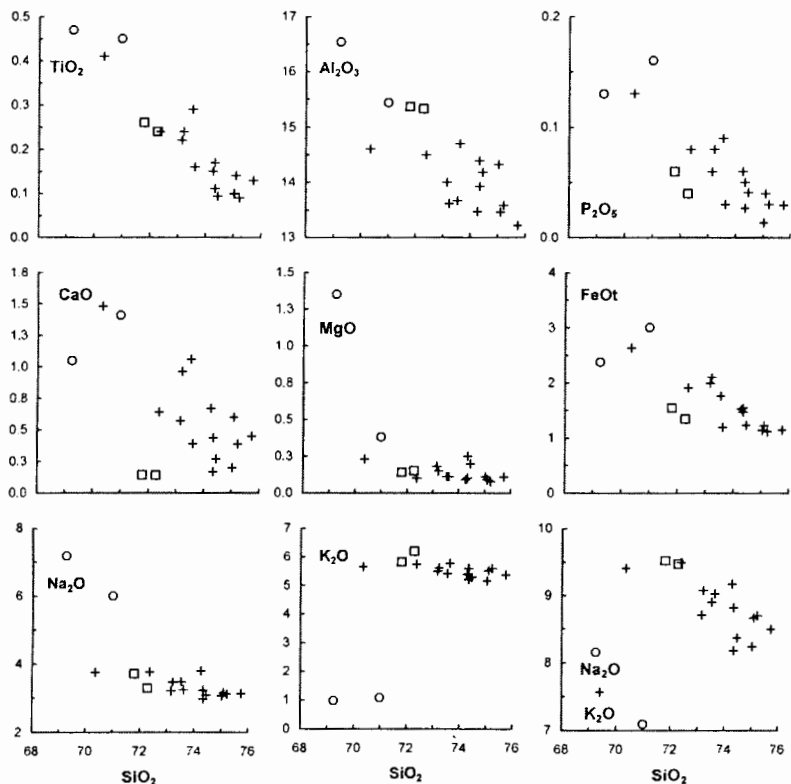
Sample Rock type	Mures (MUR) granite													Miroflio (MIR) granite			Kastanusa (KAS) granodiorite	
	MP101	MP107	MP19	MP102	MP104	MP6	MP105	MP22	MR1-4	MR1-2	MR1-8	MP23	MP21	MP5	MP112	MP111	MP12	MP13
SiO <sub>2</sub>	70.36	72.38	73.16	73.22	73.54	73.62	74.27	74.34	74.34	74.45	75.03	75.09	75.22	75.74	71.80	72.28	69.25	71.00
TiO <sub>2</sub>	0.41	0.24	0.22	0.24	0.29	0.16	0.15	0.17	0.11	0.09	0.10	0.14	0.09	0.13	0.26	0.24	0.47	0.45
Al <sub>2</sub> O <sub>3</sub>	14.61	14.50	14.00	13.62	13.67	14.70	13.47	13.93	14.39	14.18	14.33	13.46	13.59	13.23	15.37	15.33	16.54	15.44
Fe <sub>2</sub> O <sub>3</sub>	1.07	0.26	0.84	0.72	0.82	0.73	0.24	0.61	1.34	0.92	0.96	0.32	0.63	0.43	0.63	0.49	0.45	0.90
FeO	1.68	1.68	1.25	1.46	1.04	0.54	1.31	0.93	0.36	0.42	0.29	0.94	0.56	0.76	0.98	0.91	1.98	2.20
MnO	0.08	0.08	0.02	0.09	0.08	0.02	0.07	0.02	0.01	0.02	0.01	0.02	0.02	0.02	0.05	0.05	0.01	0.03
MgO	0.23	0.10	0.18	0.15	0.11	0.11	0.09	0.10	0.25	0.20	0.11	0.09	0.08	0.11	0.14	0.15	1.35	0.38
CaO	1.48	0.64	0.57	0.96	1.06	0.39	0.67	0.44	0.17	0.27	0.20	0.60	0.39	0.45	0.14	0.14	1.05	1.41
Na <sub>2</sub> O	3.76	3.76	3.21	3.47	3.48	3.25	3.79	3.23	2.97	3.08	3.07	3.15	3.12	3.13	3.71	3.28	7.18	6.01
K <sub>2</sub> O	5.65	5.73	5.50	5.61	5.42	5.78	5.39	5.59	5.21	5.29	5.17	5.52	5.59	5.37	5.81	6.19	0.98	1.08
P <sub>2</sub> O <sub>5</sub>	0.13	0.08	0.06	0.08	0.09	0.03	0.06	0.05	0.03	0.04	0.01	0.04	0.03	0.03	0.06	0.04	0.13	0.16
LOI	0.53	0.55	0.97	0.38	0.40	0.66	0.50	0.58	0.74	0.56	0.67	0.64	0.68	0.58	1.05	0.90	0.63	0.94
Total	99.99	100.00	99.98	100.00	100.00	99.99	100.01	99.99	99.92	99.52	99.96	100.01	100.00	99.98	100.00	100.00	100.02	100.00
Cr	13	19	19	14	15	5	17	6	7	6	8	3	13	8	16	13	20	15
Ni	7	4	4	9	7	2	7	2	13	15	12	2	4	3	3	7	6	4
Co	5	4	40	4	3	31	3	39	1	1	1	32	32	43	8	2	32	35
V	16	7	14	10	10	5	6	7	8	8	9	4	4	5	10	9	34	25
Rb	181	207	168	168	110	226	203	191	237	269	225	205	184	215	232	244	35	42
Ba	455	127	229	293	246	81	74	147	205	196	187	79	41	57	95	93	126	225
Sr	50	21	30	44	47	20	21	20	12	18	15	14	13	16	23	14	108	142
Nb	31	28	17	20	27	24	24	19	15	11	12	19	13	20	19	16	20	19
Zr	675	463	249	403	461	237	281	199	253	230	214	188	62	158	223	203	525	448
Y	97	84	44	67	72	70	86	45	37	47	30	59	44	66	58	58	39	36
La	62	46	46	56	50	44	44	52	45	47	33	33	48	48	39	39	53	36
Ce	120	112	107	106	109	109	108	108	75	100	84	84	96	96	57	57	53	36
Ga	25	26	22	22	20	22	24	21	18	16	19	21	21	21	24	24	110	19
Sc	10	4.6	50	32	34	34	4	3.5	7.9	50	5.7	5.7	5.7	5.7	5.7	5.7	13	13
Zn	133	50	8.5	32	34	34	7.9	50	1.7	1	1	1	1	1	8.3	8.3	9.3	9.3
Sb	3.5	5	4	3	3	3	6	3	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2	2
Cs	5	3	12	39	23	26	2.4	1.6	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2.1	2.1
Ta	3.5	3	3	3	3	3	2.4	1.6	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2.1	2.1
Hf	22	12	12	12	12	12	2.4	1.6	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2.1	2.1
Th	33	39	39	23	26	20	2.4	1.6	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2.1	2.1
U	10	9.4	9.4	23	26	20	2.4	1.6	2.4	1.6	3.2	3.2	3.2	3.2	4	4	2.1	2.1
La	66	69	69	5.8	5.6	3.1	5.8	5.6	5.8	5.6	3.1	5.8	5.6	3.1	5.8	5.6	3.1	5.8
Ce	140	150	150	120	100	93	120	100	120	100	93	120	100	93	120	100	93	93
Nd	72	64	64	53	47	41	53	47	53	47	41	53	47	41	53	47	41	41
Sm	15	13	13	11	10	9	11	10	11	10	9	11	10	9	11	10	9	9
Eu	1.6	0.5	0.5	0.3	0.2	0.2	0.3	0.2	0.3	0.2	0.2	0.3	0.2	0.2	0.3	0.2	0.2	0.2
Tb	3	2.6	2.6	2	1.7	1.5	2.6	2.6	2	1.7	1.5	2.6	2.6	2	2.1	2.1	1.5	1.5
Yb	15	13.3	13.3	7.2	6.9	6.4	15	13.3	7.2	6.9	6.4	15	13.3	7.2	6.9	6.4	15	15
Lu	2.08	1.85	1.85	1	1	1	1.85	1.85	1	1	1	1.85	1.85	1	1.29	1.29	0.95	0.95

**Table 2.** Mazor (wt%) and trace element (ppm) analyses of the Kerkini granitic complex.

respect to LREE enrichment  $[(La/Lu)_{CN}=3.5]$  but shows smaller Eu anomaly  $(Eu/Eu^*=0.62)$  and is less enriched relative to chondrite  $(La_{CN}=100)$ .

Moreover its  $\Sigma REE$  is significantly lower (150 ppm).

The MIR granite follows in general the MUR oxide trends. However, it is distinguishable in terms



**Figure 4.** Major element variation diagrams of the Kerkini granitic complex. Symbols as in figure 2.

of  $Al_2O_3$ , CaO, Nb, Zr and Y. Its REE patterns is similar to those of MUR granite with small slope  $[(La/Lu)_{CN} = 3.3]$  and strong negative Eu anomaly  $(Eu/Eu^* = 0.15)$ . MIR, however, is significantly poorer in REE compared to MUR at the same  $SiO_2$  content ( $La_{CN} = 132$ ,  $\Sigma REE = 197$  ppm). The rocks analysed are peraluminous in terms of A/CNK molar ratio which ranges between 1.0 and 1.3. Only one sample has  $A/CNK = 0.8$ .

Preliminary Sr isotope analyses gave a initial Sr ratio, based on 130 Ma, for one MUR sample of 0.7275.

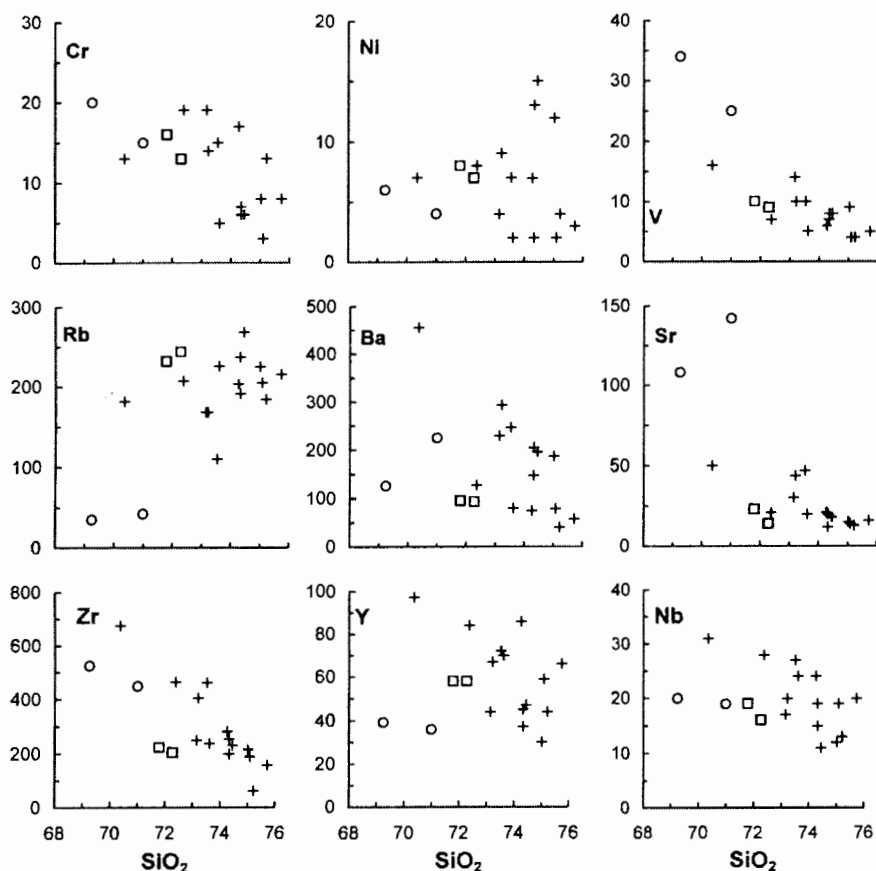
### GEOCHRONOLOGY

Three samples from MUR granite have been radiometrically dated using the K-Ar method on fresh mica separates and yielded biotite ages of  $130 \pm 3$  Ma and  $131 \pm 3$  Ma and white mica age of  $133 \pm 3$  Ma (Table 3). All three samples are fresh. Sample MP-101 is fine grained equigranular, slightly

deformed and foliated. It contains biotite with subordinate white mica. Biotite is subhedral to anhedral and contains zircons. Its contacts with quartz and feldspar are sharp. Sample MP-104 is medium to coarse grained inequigranular white mica granite. It is deformed exhibiting a gneissic texture with "augen" perthitic microcline. White mica is euhedral to unhedral with sharp contacts with neighbouring phases. Sample MP-105 has the same features with MP-104 but it is a two-mica granite.

The above ages are slightly older than the ages determined for the part of the complex situated in F.Y.R.O.M. (109 and 125 Ma with K-Ar on muscovite and biotite respectively; Karamata, pers. comm.). They are also comparable, although younger, to the ages given for the "Jurassic" granites of Axios (Vardar) zone and Serbomacedonian massif: Fanos granite -  $153 \pm 5$  Ma, K-Ar and Rb-Sr on biotite (Borsi et al., 1966);  $148 \pm 3$  Ma, K-Ar on biotite (Spray et al., 1984). Monopigado granite - "Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.



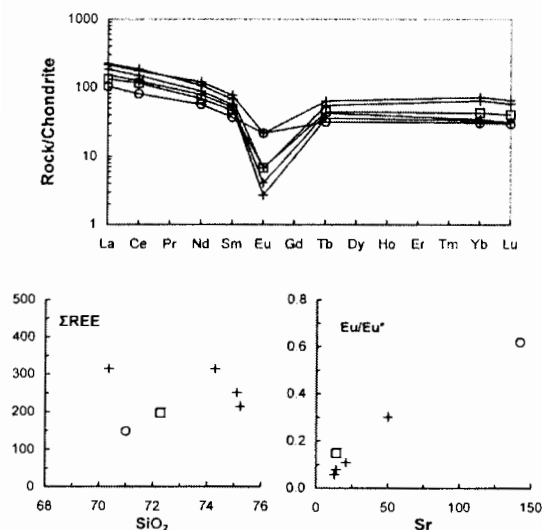


**Figure 5.** Selected trace element variation diagrams of the Kerkini granitic complex. Symbols as in figure 2.

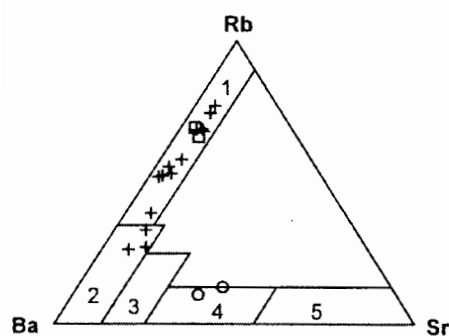
149 Ma, K-Ar on biotite (Kreuzer, in Mussallam & Jung, 1986);  $141 \pm 3$  Ma, K-Ar on biotite (Michard et al., 1998). Arnea granite -  $155 \pm 11$  Ma, Rb-Sr whole-rock (MSWD 280);  $136 \pm 1$  Ma, Ar-Ar on phlogopite (De Wet et al. 1989).

The radiometric ages for both biotite and white mica of Kerkini granitic complex are essentially identical (differing by 2 Ma), despite the 100 °C difference in blocking temperatures for the two minerals. They are very close to the Ar-Ar age on phlogopite of  $136 \pm 1$  from the Arnea granite (De Wet et al. 1989) which is geochemically similar. These similarities suggest that there was rapid cooling, either as a consequence of igneous emplacement or of rapid uplift and unroofing. How-

ever, throughout the Serbomacedonian massif of Greece, there is a general eastward decrease in radiometric ages in metamorphic rocks that has been regarded as evidence of diachronous retrograde metamorphism (Harre et al., 1968; Kockel et al., 1977) of Cretaceous age. Hercynian radiometric ages (Borsi et al., 1965) are found at the western margin of the Serbomacedonian massif but K-Ar and Rb-Sr mica ages of 102 to 131 Ma (Papadopoulos & Kiliias, 1985) were found in the Vertiscos unit. These ages were interpreted to reflect a retrograde and deformation event or a lower Cretaceous rejuvenation (Frei, 1992). The last event was considered by Sakellariou (1989) equal to the regional lower amphibolite facies meta-



**Figure 6.** REE patterns,  $\Sigma$ REE vs.  $\text{SiO}_2$  and  $\text{Eu}/\text{Eu}^*$  vs. Sr variation diagrams of the Kerkini granitic complex. Symbols as in figure 2.



**Figure 7.** Rb-Sr-Ba diagram for the Kerkini granitic complex (after Bouseily & Sokkary, 1975). 1: strongly differentiated granites; 2: normal granites; 3: anomalous granites; 4: granodiorites and quartz diorites; 5: diorites. Symbols as in figure 2.

morphic event responsible for the main structural overprint in the Serbomacedonian massif rocks. It is therefore quite possible that the radiometric ages from the Kerkini granitic complex represent an unroofing or retrograde metamorphic event. As was mentioned above several other granites in the area are attributed to the Late Jurassic and thus the Kerkini granitic complex may be part of the same intrusive episode, probably at the end of it.

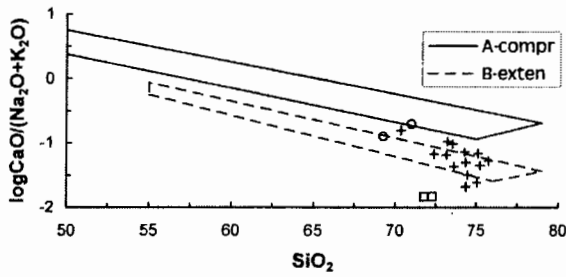
### TECTONIC SETTING

For the establishment of the tectonic setting of the Kerkini granitic complex discrimination diagrams based on both major and trace elements have been used. On Brown's (1982) diagram (Fig. 8) the analysed samples plot in field B (extensional suites). Moreover, their major element geochemistry is consistent with those of late-orogenic and anorogenic granitoids defined by Batchelor & Bowden (1985) as their plots straddle fields 4 and 5 of  $R_1$ - $R_2$  diagram (Fig. 9) with KAS samples falling definitely in field 4. In agreement with the above is their plot in the within-plate granites (WPG) field of Pearce et al. (1984) diagram (Fig. 10). Lastly, among the samples analysed for Ta and Hf the MUR granite straddles the WPG and post-COLG fields of Harris et al (1986) Rb-Hf-Ta diagram (Fig.11), the MIR granite plot in the post-COLG field and the KAS granodiorite in the WPG field. The above show that the genesis of the Kerkini granitic complex is very probably related to a within-plate tectonic setting. However, the characteristic geochemical features of the Kerkini complex

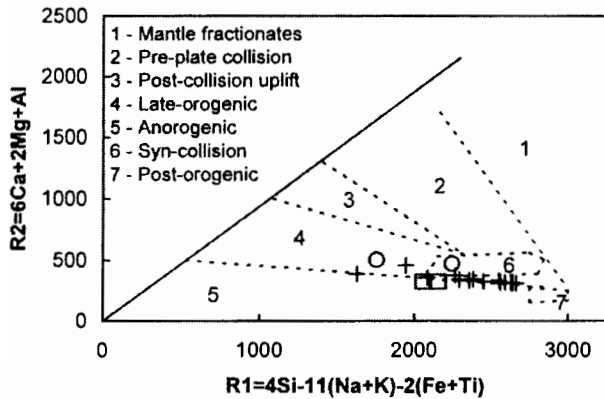
**Table 3.** Radiometric dates from Kerkini granitic complex

Sample	Component	%K	rad. $^{40}\text{Ar}$ (ppm)	Age (Ma)	Lab. No
MP-101	biotite	7.384	0.06875	130 $\pm$ 3	B-10264
MP-105	biotite	6.362	0.05986	131 $\pm$ 3	B-10266
MP-104	white mica	9.148	0.08738	133 $\pm$ 3	M-10265

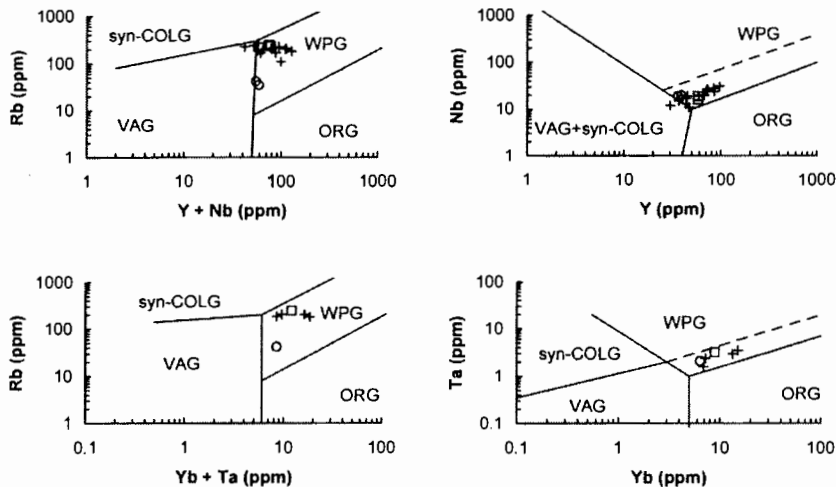
Using Steiger & Jäger (1977) decay constants



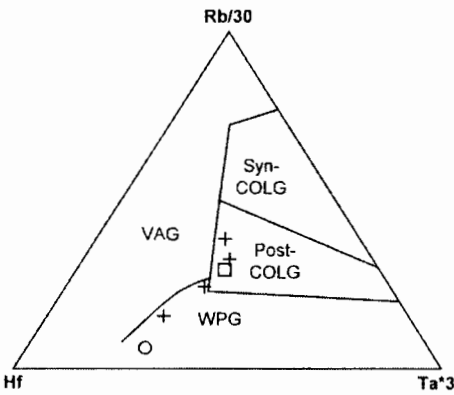
**Figure 8.** Calc-alkali index vs.  $\text{SiO}_2$  for Kerkini granitic complex (after Brown, 1982, modified by Wu and Kerrich, 1986). Symbols as in figure 2.



**Figure 9.** Plot of the Kerkini granitic complex samples on the R1-R2 diagram of Batchelor & Bowden (1985). Symbols as in figure 2.



**Figure 10.** Plot of the Kerkini granitic complex samples on the Pearce et al. (1984) discrimination diagrams. VAG: volcanic arc granites; syn-COLG: syn-collision granites; WPG: within-plate granites and ORG: ocean-ridge granites. Symbols as in figure 2.



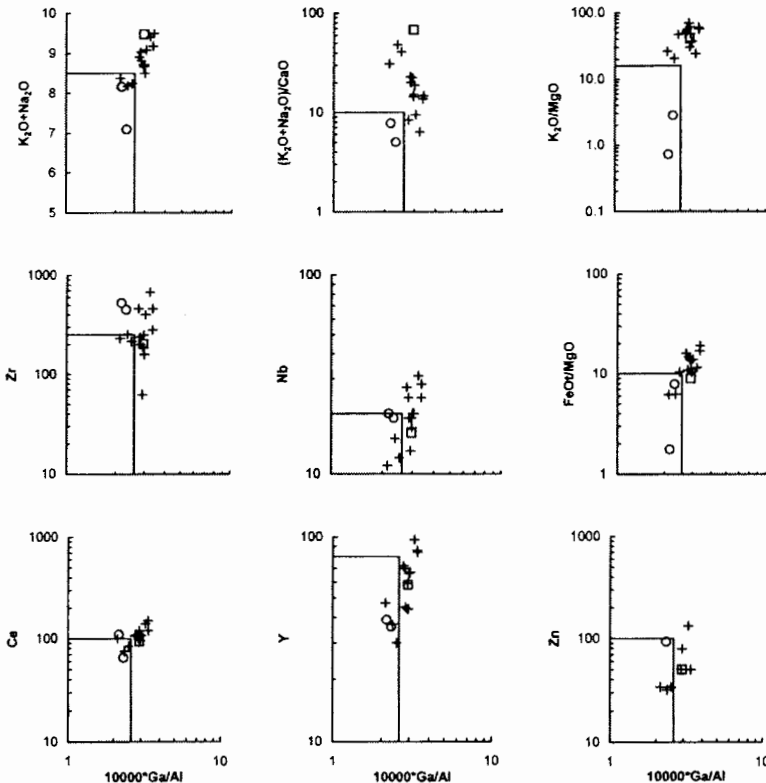
**Figure 11.** Plot of the Kerkini granitic complex samples on the Rb-Hf-Ta discrimination diagrams of Harris et al (1986). Symbols and fields as in figure 2 plus post-COLG: post-collision granites.

could be related to its source material rather than to its tectonic environment. The same is suggested for the Arnea granite by Baltatzis et al. (1992).

**DISCUSSION**

The plot of the Kerkini granitic complex in the WPG field of Pearce et al. (1984) discriminant diagram (Fig. 10) is an indication that it is related with A-type granite magmatism (Pearce et al., 1984; Whalen et al., 1987; Eby, 1990). In fact the Kerkini granitic complex has features characteristic for A-type granites as has been pointed out by many authors for various suites of such type e.g. Collins et al. (1982), Whalen et al. (1987), Eby (1990), Landenberger & Collins (1996), Mohamed et al. (1999). In particular the rocks investigated:

1. plot in the WPG field of Pearce et al. (1984) discriminant diagram,
2. are peraluminous,
3. are depleted in MgO and CaO, enriched in to-



**Figure 12.** Plot of the Kerkini granitic complex samples on the Whalen et al. (1987) discriminant diagrams. Rectangular boxes: I-, S- and M-type granites; rest field: A-type granites. Symbols and fields as in figure 2.

tal alkalis and they have high FeOt/MgO ratios,

4. are enriched in Zr, Nb, Y, Ga and REE, and they have strongly negative Eu anomaly,
5. contain iron-rich interstitial biotite (annite), and fluorite, indicating dry or almost anhydrous melts with elevated fluorine content.
6. fall in the A-type granite field of Whalen et al. (1987) discriminant diagrams  $K_2O+Na_2O, K_2O/MgO, (K_2O+Na_2O)/CaO, FeOt/MgO, Zr, Ce, Zr, Nb, \text{ and } Y$  vs  $10000 \cdot Ga/Al$  (Fig. 12) and of Eby's (1990) discriminant diagrams  $FeOt/MgO$  and  $10000 \cdot Ga/Al$  vs  $Zr+Nb+Ce+Y$  (Fig. 13a,b).

However, the pressure estimated from the phengite barometer and the absence of a contact aureole are in contrast with a high level intrusion which is a characteristic feature for many A-type granites (e.g. Collins et al., 1982; Clemens et al., 1986; Whalen et al., 1987). Here it must be emphasized that KAS granodiorite do not fulfill completely points 3, 4, 5 and 6.

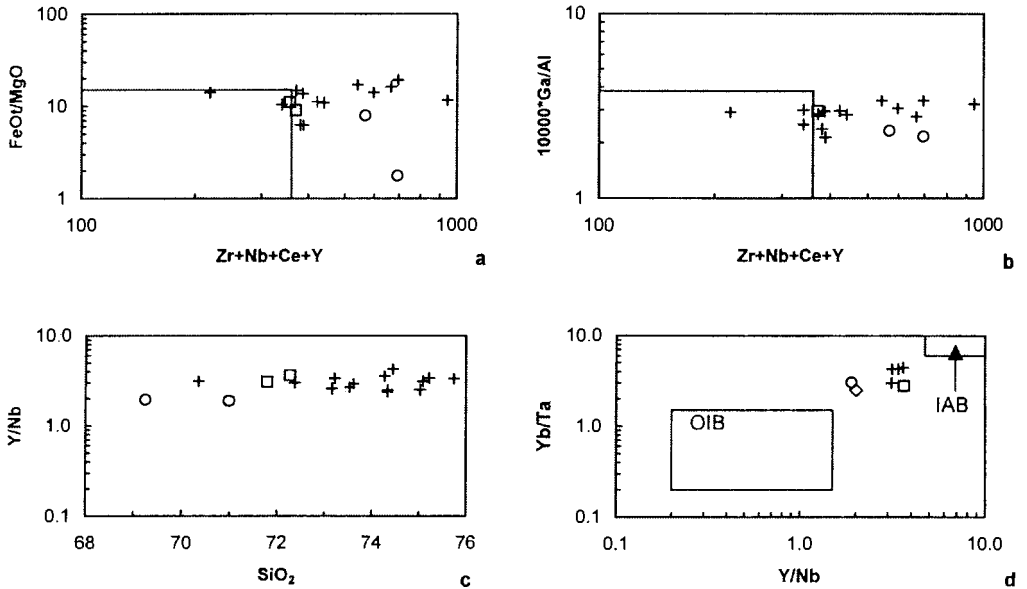
Several mechanisms have been postulated to explain the generation of A-type magmas. The major ideas that have been discussed include the following (Clemens et al., 1986, and references therein): (1) Mantle-derived alkaline magmas fractionate to produce residual granitic liquids. (2) Mantle-derived alkaline magma reacts with crustal rocks to produce a syenitic derivative that fractionates to a granitic composition or alternatively the syenitic magma further reacts with quartzose crustal rocks and eventually forms a granitic hybrid. (3) Liquid immiscibility occurs on a small scale in many basaltic liquids and has been suggested as a possible origin for peralkaline granitic magmas. (4) Liquid-state thermogravitational diffusion has been suggested as the origin of chemical variations in some A-type rhyolite magmas. (5) Fractionation of an I-type parent magma to produce an A-type residual liquid. (6) A-type magmas are the result of melting of the lower crust under the fluxing influence of mantle-derived volatiles. (7) Direct high-temperature partial melting of a depleted I-type source in the lower continental crust forms the A-type magmas. A major goal of

all these models is to explain the high absolute abundances of a number of incompatible and HFS elements and the generally  $H_2O$ -poor, but often halogen-rich, character of the magmas and the resulting rocks (Eby, 1990).

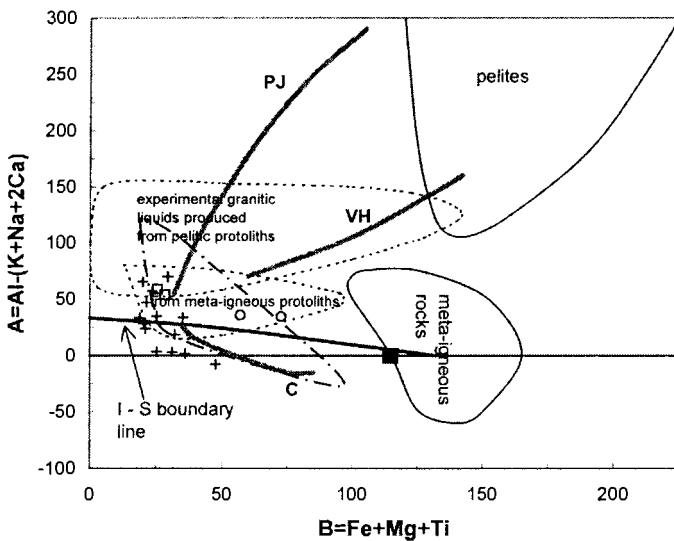
The most credible genetic model, from the above mentioned, for the origin of the A-type granites involves high temperature partial melting of melt-depleted I-type source rocks (a granulitic residue) in the lower continental crust (Collins et al., 1982; Clemens et al., 1986; Whalen et al., 1987). In such a model, melting would probably involve fluid-absent breakdown of residual, halogen-enriched micas and amphiboles. Melting could also occur in a fluid-present regime where a subcrustal source might be supply volatile species other than  $H_2O$  (Bailey, 1974; Clemens & Wall, 1981). In both cases the melts would be relatively water poor. Melting would necessarily occur at high temperature due to the relatively refractory nature of such parent materials. Recently, however, the genesis of A-type granites has been explained by partial melting of non-restitic crustal igneous rocks of tonalitic to granodioritic composition at mid-crustal pressures (Creaser et al., 1991 and Skjerlie & Johnston, 1993). An alternative model for the origin of A-type granites involves partial melting of a lower-crustal source that was dehydrated, but not geochemically depleted (Landenberger & Collins, 1996).

The Y/Nb ratio in the Kerkini granitic complex ranges from 2.4 to 4.3 and it remains constant with  $SiO_2$  increase (Fig. 13c). The Y/Nb ratio values fall within the range (1.2-7) for which Eby (1990) considered a crustal involvement in magma genesis (see also figure 13d). Sr initial ratio is high (0.7275) but no conclusions can be drawn since this value comes from only one sample.

Fluid-absent melting experiments on a biotite (20 wt%) and hornblende (2 wt%) bearing tonalitic gneiss (sample AGC150) were conducted by Skjerlie & Johnston (1993) at 6 kbar (900-975 °C), 10 kbar (875-1075 °C) and 14 kbar (950-975 °C) to study melt productivity from weakly peraluminous quartzofeldspathic metamorphic



**Figure 13.** a, b: Eby's (1990) discriminant diagrams for the Kerkini granitic complex; c: Y/Nb vs. SiO<sub>2</sub> variation diagram; d: Yb/Ta vs. Y/Nb variation diagram (after Eby, 1990). Rectangular boxes in a and b: I-, S- and M-type granites; rest field: A-type granites; OIB: ocean island basalts; IAB: island arc basalts. Symbols as in figure 2 plus diamond: average crust.



**Figure 14.** A-B diagram after Debon and Le Fort (1983) modified by Villasecca et al. (1998). Heavy curved lines: trajectories of liquids from melting of pelitic protoliths (PJ, VH) and of a metaluminous igneous protolith (C); dotted-dashed field: experimental liquids from melting of sample AGC150 (solid square) of Skjerlie & Johnston (1993). Symbols as in figure 2.

rocks. These experiments showed that the dehydration-melting of F-enriched biotite source produces F-rich granitic liquids with compositions within the range of A-type granites leaving behind a granulitic residue dominated by orthopyroxene, quartz and plagioclase. Initiation of dehydration melting is caused by intrusion of hot, mantle-derived magmas into the lower crust. The majority of Kerkini granitic complex samples plot on the A - B diagram of Debon & Le Fort (1983) fall in the field defined by the experimental liquids of Skjerlie and Johnston (1993) mostly in the part of the field

where the liquids were produced at 6 - 10 kbar and 950 - 975 °C (Fig. 14). The melting pressure is higher than the crystallization pressure calculated from the phengite barometer. Note the dispersion of the KAS granodiorite in the above field. Therefore, a similar source and a similar mechanism would give the Kerkini granites. The presence of plagioclase in the residue could explain both their strongly negative Eu anomaly and their low Sr content. Further increase of the Eu negative anomaly would be the result of plagioclase accumulation which could also explain the Sr decrease.

## CONCLUSIONS

1. The Kerkini granitic complex consist of three intrusions: the Muries granite (MUR), the Miriofito granite (MIR) and the Kastanusa (KAS) granodiorite. The main rock-type is two-mica granite.
2. Biotite is late in the crystallization sequence (interstitial) and its composition is mostly close to annite end-member. Its composition shows an alkaline to peraluminous-alkaline character for the host rock. White mica is phengite. Minimum pressure calculated from the phengite barometer ranges from 4 to 10 kbar. Fluorite is also present.
3. The rocks have features characteristic for A-type: They are peraluminous, depleted in MgO and CaO, enriched in total alkalis and have high FeO<sub>T</sub>/MgO ratios; are enriched in Zr, Nb, Y, Ga and REE, and they have strongly negative Eu anomaly; fall in the A-type granites field of Whalen et al. (1987) and Eby's (1990) discriminant diagrams and they plot in the WPG field of Pearce et al. (1984).
4. The KAS granodiorite shows a few differences in chemical composition compared with the MUR and MIR granites.
5. Sr initial ratio for one MUR sample based on 130 Ma is 0.7275.
6. K-Ar dating on micas yielded biotite ages of 130<sup>±</sup>3 Ma and 131<sup>±</sup>3 Ma and white mica age of 133<sup>±</sup>3 Ma. These ages are younger than the rest "Jurassic" granitic rocks in Serbomacedonian massif and Axios (Vardar) zone and represent an unroofing or retrograde metamorphic event of Lower Cretaceous age. The granite genesis is probably related with the Late Jurassic magmatism which gave several granites in the area.
7. The most probable genetic model for the origin of the MUR and MIR granites is fluid-absent melting of a biotite-rich tonalitic source at 6 - 10 kbar and 950 - 975 °C, leaving behind a granulitic residue dominated by orthopyroxene, quartz and plagioclase.

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