Petrology and evolution of transitional alkaline-subalkaline granitoids from Vrondou (NE Greece): evidence for fractional crystallization and magma mixing

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Abstract

The Vrondou intrusive complex is an Oligocene composite pluton, located close to the Greek-Bulgarian border, north of Serres in Central Macedonia, North Greece, which intrudes marbles and schists of the Lower Tectonic Unit of the Western Rhodope Massif. Vrondou magmas were emplaced at 7.5 to 11.2 Km depth in distinct «batches» in an extensional tectonic regime. Mafic microgranular enclaves with ellipsoidal or irregular shapes, up to 30 cm in diameter, are present only in the north-eastern part of the pluton. In the south-eastern part of the pluton a small elongated gabbro-dioritic body outcrops.

The Vrondou rocks range from gabbro to quartz monzonite having as main ferromagnesian minerals hornblende, biotite and clinopyroxene in various amounts.

The rocks as a whole cover a large compositional field, ranging from calc-alkaline to shoshonitic with some rocks falling in the field of potassic series. Two groups of enclaves are evident, one above the shoshonitic boundary and one mainly on the calc-alkaline field. On the basis of petrographic and geochemical data the rock-types fall mainly in five groups, having different genetic and evolutionary paths.

Gabbro-dioritic rocks of calc-alkaline affinity evolve through cumulus processes at low pressure in a magma chamber. Monzonitic rocks bearing high-K magmatic enclaves have a shoshonitic affinity and evolve through mixing plus fractional crystallization processes between metatuminous granodioritic-monzonitic anatexic magmas and mantle-derived magmas of lamprophyric affinity. Quartz-monzonitic rocks bearing low-K magmatic enclaves straddle the fields of calc-alkaline and high-K calc-alkaline, and evolve through processes of mixing plus fractional crystallization between anatetic magmas, similar to that of monzonite, and mantle-derived magmas of calc-alkaline affinity. Quartz syenite and granite outcropping in the south-western part evolve through various stages of fractional crystallization with different crystallizing assemblages.

The parental magmas for the strongly potassic suite were derived by partial melting of an enriched mantle wedge under different conditions of pressure and/or composition, whereas the parental magmas of the calc-alkaline suite were derived from a less enriched mantle wedge under lower pressure. Intrusions of these mantle derived melts underplate the crust, and supply heat to induce the crustal partial melting that produces metatonaceous granodioritic-monzonitic melts.

1. Introduction

Granitoid rocks are a common feature in orogenic belts and are often linked with subduction processes. However the melts were generated, the rocks carry useful information constraining the tectomagmatic events in these belts.

The magmatic activity manifested in the Rhodope massif is largely related, spatially and temporally, to the development of the Alpine orogen (Kotopoulos & Pe-Piper, 1989), which is considered to be the result of the underthrusting of the African plate under the southern European margin. This plutonic and volcanic activity began in the Upper Eocene in the northern parts of the Rhodope massif and successively shifted southwards to the Central Aegean and Western Anatolia where it continued up until the Middle Miocene (e.g. Fytikas et al., 1984; Del Moro et al., 1988; Jones et al., 1992).

In northern Greece, particularly in the Rhodope massif, there are many granitic intrusions (Fig. 1) which crosscut and overlie a wide range of supracrustal rocks of the Rhodope crystalline basement (Kolocotroni, 1992; Christofides, 1996 and references therein). In the same region, there are also volcanic products mainly, in the region north of Xanthi and in the Evros county (Innocenti et al., 1984; Eleftheriadis, 1995).

A lot of work has been done on the Vrondou complex (see references above) including several studies involving mineralogy, petrology and geochemistry. Nevertheless, the petrogenetic history of the Vrondou pluton seems to be rather complicated and far to be completely understood.

Here we present new geochemical data of Vrondou pluton aimed at understanding its origin end evolution.

2. Geology and previous work

The Rhodope massif occupies a median position between the Carpatho-Balkan branch, in the north and the Dinaride-Hellenide branch, in the south of the Alpine orogenic belt. It extends along the Bulgarian-Greek borders covering large areas of both countries as well as a small part of north-western Turkey (Fig. 1). In the Greek territory the
Rhodope massif to the west abuts the Serbomacedonian massif, along the «Strymon line» fault and to the south and south-east it is bounded by the Circum-Rhodope belt. Extensional tectonic forces resulted in the formation of fault-controlled sedimentary basins in the Rhodope massif (Maltezou & Brooks, 1989).

Rhodope massif is separated into distinct geological units by major thrust zones. Thus, Western and Central Rhodope, on both lithostratigraphic and structural criteria, form an Upper Tectonic Unit (UTU – Sideroneron Unit) and a lower Tectonic Unit (LTU – Pangeon Unit) separated by an approximately SSE-NNW striking thrust plane (Papanikolaou & Panagopoulos, 1981).

Early to Middle Eocene regional amphibolite facies metamorphism (Liati, 1988) overprints earlier high-pressure facies metamorphism recorded by eclogitic amphibolites in central and eastern Rhodope. A retrograde green-schist facies metamorphism is seen in amphibolites, metapelites and gneisses (Liati & Mposkos, 1989). A post-metamorphic magmatism produced the Tertiary extrusive and intrusive rocks outcropping in Rhodope massif.

The deformation history of the Rhodope massif is very complicated. In general, two stages of deformation have been recognized: an early SW-directed syn-metamorphic shearing and a post-metamorphic imbrication (Kilias & Mountrakis, 1990; Dinter et al., 1995 and references therein).

The Vrondou complex (Fig. 1) is located close to Greek-Bulgarian border, north of Serres in Central Macedonia, North Greece. It is a north-eastwards elongated composite pluton (covering more than 250 Km²) intruding gneisses, amphibolites and marbles of the Lower Tectonic Unit of the Western Rhodope massif. Small and large pockets of the crystalline basement, ranging up to several tens of meters, are found within the pluton, especially in the southern part. To the eastern and north-eastern margins of the pluton a clear contact aureole has been developed (Kolocotroni, 1992 and references therein).

The pluron is, in general, undeformed. However, the southern and western parts are slightly to intensively deformed by a flat-lying shear system, which has led to mylonitic foliation and SW-plunging stretching lineation (Kolocotroni, 1992). The resulting gneissic texture becomes progressively more clear towards the southern margins. Recrystallized quartz, feldspars and mafic minerals are a common feature of the more deformed rocks.

The field relations of the various rock-types are rather obscure, apart one case in the eastern part of the pluron where a sharp contact between a medium-grained granodiorite and a coarse-grained quartz monzonite was found. In the same area Papadakis, (1965) described the intrusion of a monzonite into granodiorite.

Leucocratic dykes, mainly plagioclase and occasionally pegmatitic, are encountered throughout the entire plutonic body. In contrast, microgranular enclaves with ellipsoidal or irregular shapes, up to 30 cm in diameter, are present only in the north-eastern part of the pluron. A small elongate gabbro-dioritic body with sharp contacts with the granodiorite outcrops in the south-eastern part of the pluron. Rounded to angular blocks of diorite are enclosed in the granodiorite with a similar aspect to magmatic breccia. In some cases gabbro shows clear cumulate features. Finally, hornblende-rich lamprophyric dykes occur in the southern margins of the pluron (Kolocotroni, 1992).

Based on geological data, Osswald (1938) suggested an Eocene age for the Vrondou pluton, like other Macedonian granites. Papadakis (1965) supported the above age on the basis of K/Ar dating on a hornblende separate (54.9±4.2 Ma), whereas an Oligocene age was obtained with the same K/Ar method on hornblende (34±2 to 30±1 Ma; Marakis, 1969) and biotite (30±3 Ma; Dürr et al., 1978) separates. A similar age (30.8±14.8 Ma) based on Rb-Sr whole-rock data was accepted by Kolocotroni (1992), although the error is considered high. It must be noted here that Meyer & Pilger (1963) suggested an older age for the western part of the Vrondou pluton, thus supporting a non
simultaneous formation. In contrast, Kaufman (1995) suggested a mid-Oligocene emplacement age for the eastern undeformed part of the Vroudon pluton, while the strongly monolithic western part may have been emplaced in earliest Miocene time.

3. Petrography

On the normative Q-ANOR classification diagram (Fig. 2A; Streckeisen & Le Maitre, 1979), preferred because of the coarse-grained and porphyritic texture of most Vroudon rocks, the rocks classify as quartz monzonite, granite (granite + monzogranite), granodiorite, monzonite, quartz monzodiorite, quartz syenite, diorite and gabbro. These rock-types are in good agreement with the modal classification of selected samples. A summary of the petrographic features of the Vroudon rocks is reported in Table 1.

Gabbro (GB) is medium- to coarse-grained and contains plagioclase, amphibole, clinopyroxene and occasional olivine and orthopyroxene. Diorite (DR) is fine- to medium-grained containing plagioclase, hornblende and biotite.

Monzonite is usually coarse-grained and equigranular exhibiting locally strong porphyritic texture with large K-feldspar phenocrysts. It outcrops only in the eastern part of the pluton. Apart from the abundant K-feldspar it contains plagioclase, clinopyroxene, hornblende and in some cases subordinate biotite. Quartz monzonite is coarse-grained, showing often porphyritic texture. It mainly outcrops in the eastern part of the pluton surrounding monzonite. It changes gradually to granodiorite. Quartz monzonite mainly consists of plagioclase and hornblende and subordinate K-feldspar, quartz and biotite. Clinopyroxene occurs in some samples either as single crystals or as relics in hornblende cores. Quartz monzodiorite is similar to the clinopyroxene-bearing quartz monzonite differing only in the mineral proportions.

Granodiorite is medium- to coarse-grained occurring mainly in the central-northern part of the studied area, and as small masses in other places. Plagioclase, quartz and hornblende are the predominant phases, while biotite appears in subordinate and less often in equal amounts with hornblende.

Granite, like granodiorite, is medium- to coarse-grained, but lighter in colour than granodiorite. It mainly covers the south-western part of the pluton together with some local quartz syenite and granodiorite transitions. Mostly, it is slightly to intensively deformed. Granite contains plagioclase, quartz, K-feldspars and biotite, which in most samples is the only ferromagnesian mineral. Hornblende usually occurs in subordinate amounts.

Quartz syenite has the same mineralogy with granite except that hornblende is the main or the only ferromagnesian mineral.

Titanite, apatite, zircon and opaques are the main accessory phases in almost all rock-types there. In the gabbro spinel is also present.

Based on petrographical and geochemical data the above rock-types are mainly grouped in the following groups:

1) GBDR: gabbros and diorites bearing hornblende, clinopyroxene, and rare olivine and orthopyroxene;
2) MZ: monzonites, clinopyroxene-bearing quartz monzonites, and quartz monzodiorites with clinopyroxene + hornblende ± biotite;
3) QMZ: clinopyroxene-free quartz monzonites and granodiorites with hornblende + biotite;
4) QSY-GR: quartz syenites with hornblende ± biotite and granites with biotite ± hornblende;
5) GD: some granodiorites and granites with hornblende + biotite.

In general, the rocks of the MZ and QMZ groups occupy the NE part of the Vroudon pluton, whereas those of the QSY-GR and GD groups cover the SW part.

As mentioned in the section of regional geology, abundant mafic microgranular enclaves occur in the plutonic rocks of the eastern and north-eastern parts of Vroudon. The enclaves almost always have the same mineral assemblage present in the host rock and are more fine-grained,

Table 1 – Main petrographic features of the Vroudon plutonic rocks.

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Fig. 2 – Q′-ANOR diagram (A; after Streckeisen & Le Maitre, 1979) and K₂O vs SiO₂ diagram (B; after Peccerillo & Taylor, 1976) of the Vroudon plutonic rocks; dashed lines in B connect enclaves with their host rocks.

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holocrystalline rocks with equigranular subophitic matrix. They mainly classify as diorite and monzodiorite consisting of plagioclase + hornblende ± clinopyroxene ± biotite ± K-feldspar + accessories. In general, the enclaves are distinguished into two types on the basis of potassium content and their mafic minerals. The first type (Low-K MME) contains abundant hornblende and subordinate biotite, while the second type (High-K MME) consists of hornblende and clinopyroxene, with clinopyroxene occurring as independent crystals and/or as relics in hornblende cores. The latter group is characterized by the presence of abundant K-feldspar, which poikilitically includes the other phases.

Mineral chemistry is based on our new unpublished data (for clinopyroxene, hornblende and biotite) as well as on Kolocotroni (1992) and Theodorikas (1982) data (for feldspars, orthopyroxene and olivine).

Plagioclase, of oligoclase to labradorite composition, occurs in all rock-types, constituting the most abundant phase. It is medium to coarse-grained, euhedral to subhedral. Apart from the plagioclase of the gabbroic rocks, which are unzoned, all other plagioclase exhibit slight to extensive normal and oscillatory zoning, and not rarely patchy cores. Fine-grained, euhedral plagioclase occurs as inclusion in K-feldspars. Thin bands of myrmekite develop between plagioclase and K-feldspar in the more evolved rocks. K-feldspar occurs as a groundmass mineral and as mega-crysts in the porphyritic rocks reaching up to 5 cm long. It appears in euhedral to subhedral crystals, but also as irregular crystals poikilitically including all other phases. Often, K-feldspar is twinned after in the Carlsbad law. Usually, in the quartz-bearing rocks it is microcline, whereas in monzonite it is orthoclase. Not uncommonly, K-feldspar contains inclusions of plagioclase and mafic minerals.

Amphibole is the most abundant and ubiquitous ferromagnesian phase. It forms euhedral to subhedral crystals of green-brown colour, and it is classified, mainly, as magnesio-hornblende and less as tschermakitic, edenitic and magnesio hastingsitic hornblende (Leake, 1978). In some monzonitic and quartz monzonitic rocks from the eastern and north-eastern parts of the pluton hornblende preserves clinopyroxene cores. Amphibole in the gabbro poikilitically encloses all other phases.

Biotite is the second most abundant mafic mineral increasing modally in the more differentiated rocks. In samples with SiO2, more than 70% it is the only ferromagnesian mineral. Biotite exhibits euhedral to subhedral crystals brown to straw yellow in colour. In some monzonitic rocks biotite occurs as very fine rounded inclusions. Biotite is partly altered to chlorite. Compositionally biotite from clinopyroxene-bearing monzonte is more Ti- and Mg-rich (mg#>60) than that from other rock-types (mg#<60).

Clinopyroxene, of diopside composition (Morimoto et al., 1988), mainly occurs in gabbroic rocks, coexisting with amphibole, and in monzonte and some quartz-bearing monzonte, coexisting with hornblende and/or biotite. It appears as independent euhedral to anhedral crystals and as irregular relics of variable size in hornblende. Moreover, clinopyroxene alter to actinolitic amphibole along cleavages or marginally.

Orthopyroxene and olivine (mainly transformed in serpentine) occur only in the gabbroic rocks in subordinate amounts. Both minerals appear in euhedral to anhedral crystals and in symplectic intergrowths with opaque oxides. Orthopyroxene is enstatite on the basis of Morimoto et al. (1988).

### 4. Whole rock chemistry

As already pointed out, the rocks from Vrontou cover a large compositional field, ranging from calc-alkaline to shoshonitic with some rocks reaching the field of potassic series, on the Peccerillo & Taylor (1976) diagram (Fig. 2B). Such a large spectrum is mainly defined by the basic-intermediate rocks: gabbro-dioritic rocks plot on the boundary between calc-alkaline and high-K calc-alkaline fields except for one sample; two groups of enclaves are described, one with K₂O>2.5% (High-K MME) above the shoshonitic boundary and one with K₂O<2% (Low-K MME), mainly on the calc-alkaline field; the less evolved of the MZ and QSY-GR rocks plot well above the shoshonitic boundary. In figure 2B tie lines connecting enclaves with their relative hosts are depicted. It is noteworthy that low-K MME have been found in the QMZ group, whereas High-K MME have been found in the MZ group.

The Vrontou rocks plot on the calc-alkaline field of the AFM diagram (Irvine & Baragar, 1971; not shown) and they define a typical late-oregenic suite with low TiO₂, Ta and Nb abundances. However some rocks plot in the alkaline field of the K₂O+Na₂O vs SiO₂ diagram (not shown): the more basic rocks of the QSY-GR group and of the MZ group, and the High-K enclaves. Despite this alkaline tendency all the Vrontou rocks plot in the VAG field of the Rb vs Yb+Ta and Nb vs Y diagrams (Fig. 3).

![Fig. 3 - The Vrontou plutonic rocks plotted on the Rb vs Yb+Ta (A) and Nb vs Y (B) discrimination diagrams of Pearce et al. (1984). VAG, volcanic-arc granites; syn-COLG, syn-collision granites; WPG, within-plate granites; ORG, ocean-ridge granites. Yb and Ta are unpublished data. Symbols as in figure 2.](image-url)
Samples from the strongly deformed area at the southern extrem, consisting of a gneissic matrix, overlap geochemically with the rest of the Vroudon samples that do not show any metamorphic signature at all. This feature coupled with field constraints, such as the gradational contacts between the deformed and the non-deformed rocks, having gneissic and intrusive textures respectively, suggest syn-intrusion deformation that may be considered as isochronal.

Major element variations

Chemical compositions of selected samples are reported in table 2. Major and trace element variation diagrams using CaO as a differentiation index are shown in figure 4.

Table 2 – Chemical analyses of selected samples from the Vroudon pluton.

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</tr>
<tr>
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<td>52</td>
<td>52</td>
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<tr>
<td>Ce 23</td>
<td>23</td>
<td>23</td>
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<td>65</td>
<td>81</td>
<td>87</td>
<td>74</td>
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</table>

See text for explanation. $^{a}$ recalculated to give constant 100.00±0.01 sum.
Major elements (exclusive of Na2O and LOI determined by wet chemical analysis) analyzed by XRF with full matrix correction after Franzini et al. (1972); trace elements by XRF after Kaye (1986). The precision is better than 10% for V, Cr, Ni, X, Zr, and Ba, and better than 5% for all other elements. The accuracy has been tested on international standards and is better than 10%.

Some aspects of the geochemical behaviour of the rocks are pointed out below.

GBDR: these samples have similar SiO2, MgO, K2O, CaO (except for one sample), Na2O (except for one sample), P2O5 and TiO2 (except for two samples).
MME: Low-K and High-K enclaves show roughly the same range for SiO$_2$, Al$_2$O$_3$ (except for one High-K sample with very low value), MgO and P$_2$O$_5$. High-K MME have clearly higher K$_2$O and lower Na$_2$O (see also table 2) and broadly lower FeO and TiO$_2$, than the Low-K MME.

MZ: SiO$_2$ ranges from 56 to 65% and the samples have quite scattered trends on all variation diagrams. On the P$_2$O$_5$ vs CaO diagram two groups of samples can be distinguished with different P$_2$O$_5$ contents at similar CaO content.

QMZ: SiO$_2$ ranges from 62 to 69% and rocks are quite scattered on many diagrams and plot in the intermediate fields for many elements.

QSY-GR: SiO$_2$ ranges from 56 to 75%. All samples plot along well defined trends for SiO$_2$, TiO$_2$, FeO, MgO, and P$_2$O$_5$. With respect to the other groups they have higher contents for all the elements but silica at the same CaO values.

GD: These clearly do not plot on the QSY-GR trends, but define their own trends resembling those of the other groups, even with a narrow SiO$_2$ range of 64-71%.

Trace element variations

Ferramagnesian elements, except Co, show some scattered trends for all the rock groups. Noticeable is the high content of Cr, and to some extent Ni, in the MZ group. Rb is quite scattered with samples from the MZ group having higher contents at the same CaO values. Ba behaves compatibly in the QSY-GR groups whereas it is very scattered in all the other groups with the MZ samples likewise having the higher contents. The same holds, at higher CaO, for High-K enclaves and GBDR (apart from one sample). High field strength elements (Zr, Nb, Y) show good correlation with CaO for QSY-GR samples, whereas the other samples are quite dispersed with characteristic behaviour for particular samples. Unusual is the behaviour of the Low-K enclaves for Y. They have a very large range from 11 to 47 ppm outside analytical error. On the other hand the same samples have no cumulitic accessory phases such as zircon or titanite as indicated by their lower abundances of Nb (except for one sample) and Zr, La, Ce, and Th have scattered patterns, even if a roughly trend can be recognized again for the QSY-GR group.

5. Discussion

The whole-rock geochemical, and petrographical data from the Wrondou pluton lead to some primary observations:

1) In samples from the NE area, plagioclase displays complex zonation pattern with patchy textures, and clinopyroxene (where present) may occur as relics enclosed within hornblende cores. In addition, other textures claiming for magma mixing, for example acicular apatite, spike zones in plagioclase (Hibbard, 1991) are often found.

2) The south-western part of the pluton (QSY-GR and GD groups) can be easily distinguished from the other parts
on the basis of: (i) the less evolved rocks are quartz syenite; (ii) MME are not present at all in this area; (iii) QSY-GR rocks have higher Sr, Ba, and to a lesser extent Zr, Y, Nb, La, Th, and Ce; (iv) QSY-GR rocks have (Tb/Yb) > 1, whereas all the other rocks have mainly (Tb/Yb) < 1 (unpublished data). Petrography and geochemistry are also helpful in distinguishing the other groups: (i) MZ group bears clinopyroxene and amphibole, whereas QMZ bears amphibole alone; (ii) Low-K MME have been found in the QMZ group, whereas High-K MME have been found in the MZ group; (iii) QMZ rocks have much more evolved compositions than the MZ rocks.

3) The presence of abundant titanite and zircon can also be recognized in the geochemical space, mainly in the groups outcropping in the north-eastern part of the pluton even if the amount of these phases is not dramatically different from that in the western part. This indicates a much complex petrogenetic process for the MZ and QMZ rocks, than for the QSY-GR and GD rocks.

In this section, we discuss the implications of these observations. First, we discuss the petrogenesis of the more basic rocks (GBDR and MME) because this is preliminary to the other parts. Second, we propose a two-step fractional crystallization model for the evolution of the QSY-GR group which is characterized by an enrichment and variability in certain major and trace elements. Third, a mixing/fractional crystallization (MFC) model is addressed to elucidate the geochemical characteristics of the MZ and QMZ groups. Finally, we discuss in brief the generation of the parental magmas and evaluate the possibility of deriving these magmas by crustal melting or from an enriched mantle.

**GBDR and MME**

The textures of the gabbro-dioritic rocks as well as their geochemical characteristics, e.g. the high Ba, Sr, Y and the low Co, Nb, Na2O contents (Table 2), indicate that the main differentiation process in these rocks was crystal accumulation of feldspars and accessory minerals together with trapping of residual liquid. Cumulus processes of main and accessory phases are the rule and not the exception in differentiation mechanisms of basic complexes (e.g. McBirney & Noyes, 1979; Irvine, 1980; Cawthorn, 1996). Although GBDR rocks are not considered as true liquids, due to their cumulitic character, they are still important in understanding the evolution of the Vrondou pluton. Low-K enclaves, in fact, mimic quite well the pattern followed by the GBDR rocks, so these enclaves could represent fragments of basic magma incorporated into acid magma, according to the model proposed by Poli & Tommasini (1991).

Concerning the two groups of enclaves (High-K and Low-K MME), questions arise in defining their geochemistry because they are not different, for the same level of K and Rb, for all the other major and trace elements except Ba (Fig. 5). One explanation in that behaviour could be phase accumulation processes. In figure 5 normalized values are reported for literature data of K-feldspar and biotite together with averages of the two types of enclaves. It is clear that the geochemical features of the two groups of enclaves could not be achieved by mixing processes between a magma with less K content and those minerals. In addition, it is noteworthy that petrography also rules out this possibility because High-K MME have really low modal abundance of biotite and K-feldspar. On the other hand the two groups cannot have been derived from each other through processes at shallow level. In order to increase the K2O, Rb, and Ba contents of a factor of more than 4 by crystal fractionation, and assuming a meaningless zero value for Ba and Rb bulk partition coefficients, fractionation values (1-F) more than 80% and 62% respectively are necessary. This contrasts with all the other geochemical features, e.g. on average the two groups of MME have the same values of SiO2 and compatible elements. These conclusions support the hypothesis that two parental magmas with different affinity, typical calc-alkaline and shoshonitic, coexist in the Vrondou area. Although the presence of typical shoshonitic magma is well established, the presence of magmatism with K2O as high as that of the High-K enclaves is not so common in the Rhodope massif. However, Kolocotroni (1992) reported the presence of rocks with lamprophyric affinity in the southern part of the Vrondou area characterized by strong enrichments in K2O, Rb, and Ba but relatively poor in LILE and HFSE. The range of values of those lamprophyres is shown in figure 5 (hatched area). It is important to note the similarity of the patterns among High-K MME and lamprophyres, taking into account the fact that lamprophyres are far less evolved that MME. In addition, RREE patterns of lamprophyres and MME High-K are similar for light and heavy RREE fractionation and Eu anomaly (Kolocotroni, 1992 and unpublished data). All these features indicate that MME High-K can be considered as slightly evolved magmas from lamprophyric parental sources.

**QSY-GR and GD groups**

The decrease in Sr, Ba, and scattered uniformity of Rb with differentiation within QSY-GR group are consistent with fractionation of abundant amounts of feldspar and relatively small amounts of biotite. Ferromagnesian elements decrease continuously except Co and Cr that are quite scattered, all indicating fractionation of amphibole. As regard HFSE, they are consistent with fractionation of both zircon and titanite, because of strongly decreasing of Zr, Nb, Y, and Hf (unpublished data).
Following this line of reasoning, we have modelled a FC process using the less evolved QSY-GR sample (TS4; tables 2 & 3) as parental magma. As is evident in figure 6 a single process of FC cannot explain all the range of compositions of QSY-GR group, because: (i) changes in the evolution trend occur for many elements at intermediate compositions, and (ii) 100% of fractionation is reached for many elements without reaching the more evolved compositions. A two-step FC process is much more likely and we modelled it using the more evolved quartz syenite sample (L2; tables 2 & 3) of the QSY-GR group as parental magma for the second step. The bulk distribution coefficients (D, table 3) were determined in order to reproduce the compositions of the QSY-GR group (Fig. 6). In addition, a quantitative estimate has been made in order to obtain the fractionating mineral assemblages using a partition coefficient mixing computation (table 3). Starting from the modelled bulk partition coefficients and using partition coefficients reported in Appendix, the percentage of single minerals have been calculated by linear programming minimizing the sum of squares of residuals as a constraint (e.g. Wright & Doherty, 1970). For the first step of the FC process the modelled bulk distribution coefficients are consistent with fractionation of plagioclase + amphibole + biotite, and subordinate quantities of K-feldspar and apatite, titanite and zircon (table 3). The second step involves a smaller amount of amphibole + biotite and an increase of plagioclase in the fractionating assemblage. Such assemblages are in very good agreement with the petrographic features for the QSY-GR group. It is important to note that some deviations exist for some elements (e.g. Th, Nb, Fig. 4) which can be explained by possible variations of the initial compositions of the two parental magmas used in the calculations. This could also explain the imperfect matching of the calculated and the observed bulk partition coefficient for Th.

Scarcity and patchy occurrence of the GD-group prevent a detailed investigation. Some constraints are possible. The range of SiO$_2$ is similar to that of the QSY-GR group, and the same holds for the geochemical behaviour of many elements, except for Sr, Zr, Nb, and Y. These features could be in accord with different amounts of fractionated minerals during the same crystal fractionation process as for QSY-GR group. In particular the smaller depletion of those elements could be explained by a smaller amount of feldspar (Sr), zircon and titanite (HFSE) in the fractionated assemblage.

**MZ and QMZ groups**

The presence of enclaves and petrographic features point to a mixing between at least two magmas during the evolution of these rocks. In addition, a closed system FC process is ruled out by isotopic data (Kolocotronis, 1992). Differentiation is thus primarily due to a mixing process. However, this cannot be a simple two end-member mixing as geochemical features do not show any pattern connected with such a process, e.g. linear trends in element element diagrams. Therefore a process of mixing plus fractional crystallization is proposed for samples from NE area. Between the MZ and QMZ groups, there are differences in the less evolved samples both from petrographical and geochemical points of view, but also very similar geochemical features for the more evolved rocks (Fig. 4). Accordingly, the variation could be explained using similar acid end-members for the two groups in the mixing process, but a different basic end-member.

With regard to the basic end-member, the enclaves, considered representative of evolved basic liquids (e.g. Poli et al., 1996), have peculiar features: Low-K MMF have
been found in the QMZ group only, whereas High-K MME have been found in the MZ group only. Therefore the two groups must have different basic end-members. Regarding the MZ group, the tight similarity between High-K MME and lamprophyres from the southern Vrondou area, lends to support the hypothesis that lamprophyres could represent the end-member for this group. Much more difficult is the recognition of the basic end-member for the QMZ group because gabbron-dioritic samples, due to their cumulate character, may not be typical of a true basic calc-alkaline liquid and no other such magmas are present in the Vrondou area. Instead of using magmas obtained from well away from the Vrondou area, we prefer to model the MFC process using an average of the less evolved Low-K MME as the basic end-member. This is not completely correct, but the point of the proposed MFC model is not to rigorously constrain r values and bulk partition coefficients (De Paolo, 1981), nor do we claim that every point should fall on the modelled MFC trends, but to define possible ranges for magma evolution as contaminated by the acid end-member.

Model for the MZ group: Following this line of reasoning, we have modelled an MFC process using an average of lamprophyres (Kolocotroni, 1992) as the starting composition and the sample of QMZ group poorest in compatible elements (SB9; tables 2 & 4) as the acid end-member (Fig. 7A). The bulk distribution coefficients (D) and the ratio of contamination rate/crystallization rate (r) (as defined by De Paolo, 1981) were determined in order to reproduce the range of compositions of the MZ group (Fig. 7A). Two sets of D values at constant r are necessary to model the MFC process, and they have been reported in Table 4. The modelled bulk distribution coefficients, are consistent with fractionation of clinopyroxene + plagioclase + K-feldspar, subordinate quantities of amphibole + biotite, and accessory apatite, titanite and zircon. This fractionating assemblage is consistent with petrography, and the presence of biotite as a fractionating mineralogical phase is consistent with the evolution of the basic magma by means of a process of contamination by the acid magma (e.g. Watson & Jurewicz, 1984). It is noteworthy that the ratio between the assimilated mass and fractionated mass (Aitcheson & Forrest, 1994) remains lower than 25% also for the more evolved rocks.

Model for the QMZ group: We performed the same type of modelling and the results are reported in Table 4 and Figure 7B. The modelled bulk distribution coefficients are consistent with fractionation of amphibole + biotite + plagioclase + K-feldspar, and accessory apatite, titanite and zircon. Lack of clinopyroxene is consistent with the petrography of Low-K MME. For this group the ratio between the assimilated mass and fractionated mass (Aitcheson & Forrest, 1994) remains lower than 15%, also for the more evolved rocks.

Conclusive remarks on the evolutionary history of the different Vrondou rock-groups can be given. Although the modelled processes are well constrained for many elements even with different geochemical behaviour, and the amount of crystallization and assimilation is very reasonable, it is noteworthy that some dispersion exists for some samples within all the groups. This can be explained by possible variations in the composition of the basic and acid magmas, and/or some problems in recognizing a small accumulation of accessory minerals, and therefore, those models provide a reasonable explanation for the compositional variability of the Vrondou samples.

**Genesis of parental magmas**

Although it is beyond the aim of this work, and also because none of the more basic samples is primary but has certainly been affected by evolutionary processes, the genesis of parental magmas of the different groups of Vrondou pluton can be briefly discussed.

Intriguing is the genesis of the parental magma of the QSY-GR group. Similar types of magma found in different areas and with different ages, e.g. Western Alps (Valle del Cervo pluton, 30 Ma; Bigioggero et al., 1996) and Corsica (Mg-K series, 320 Ma; Cocherie et al., 1994) are unknown in the Rhodope massif. In contrast rocks like the MZ group are well known (Xanthi, Christofides, 1977; Maronia, Del Moro et al., 1988). The mantle/crust genetic dichotomy is evidenced in the author views of the two former papers: Bigioggero et al. (1996) suggest a mantle enriched wedge as the source of the Valle del Cervo pluton, whereas Cocherie et al. (1994) propose a crustal rock of graywacke composition as the source of the Mg-K series. Although our data are insufficient to enter into a deep discussion, we wish to stress some features. Experimental petrological data, recently reviewed by Johannes & Holtz (1996), preclude any possibility that graywackes can be the source of metaluminous melts such as the rocks under study; on the contrary, amphibolitic sources can give metaluminous melts, but not high-K melts with silica values of basalt or basaltic-andesite. Roberts & Clemens (1993) proposed hydrous calc-alkaline to high-K calc-alkaline, mafic to intermediate metamorphic rocks in the crust as a possible source for these mafic high-K magmas. Although it is impossible to rule out this possibility, it seems at least an ad hoc hypothesis that shifts the problem back to the past. A hypothesis alternative to anatexis of a crustal source in generating such types of magmas is a partial melting of an enriched upper mantle. Low isotopic Sr data from the same area (Kolocotroni, 1992) lend to support this hypothesis.

Regarding the High-K MME, the genesis of lamprophyric rocks is very much debated (Mitchell & Bergman, 1991 and discussion therein), but a first order agreement exists for lamprophyric genesis by partial melting of an enriched phlogopite-bearing mantle source. Mica analyses from the lamprophyric dykes are not available, but the tendency of biotite in monzonite (MZ group in this paper) to become progressively more Mg- and Ti-rich, that is a

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**Table 4** Parameters used in the mixing/fractional crystallization models for the MZ and QMZ groups.

<table>
<thead>
<tr>
<th>MZ Group (r=0.35)</th>
<th>QMZ group (r=0.2)</th>
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<tbody>
<tr>
<td>C_M</td>
<td>C_A</td>
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<tr>
<td>V</td>
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<tr>
<td>Y</td>
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</tr>
<tr>
<td>La</td>
<td>49</td>
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</table>

C_M: composition of initial basic magma in ppm (MZ group, average of lamprophyres, Kolocotroni, 1992; QMZ group, average of less evolved Low-K MME); C_A: composition of contaminant acid magma in ppm (sample SB9); D: Two sets of modelled bulk distribution coefficients for MFC process; r: assimilation rate/crystallization rate.
clear phlogopitic trend, indicates that phlogopite could be a liquidus mineral for this kind of rocks (Kolocotronis, 1992). Thus, it can safely be supposed that High-K MME are evolved rocks derived from partial melting of an enriched mantle source without or with minimal crustal interaction.

The source of the acid end-member of the MFC processes can be easily located in a middle-lower crust of amphibolitic composition (Johannes & Holz, 1996), even if the very high K, O content and the relatively low normative quartz, indicates a role of biotite in the melting process.

6. Conclusions

The complex petrogenetic history of the Vrondou pluton can be associated to multiple interaction between mantle and crust derived magmas in an active continental margin environment.

At least four different parental magmas have to be proposed in the genesis of the Vrondou complex: the more basic rocks of the QSY-GR group outcropping in the southwestern area; the shoshonitic lamprophyres outcropping in the southern area, and believed to be the precursor of the High-K enclaves; the gabbro-dioritic rocks outcrop-
monzonite, were derived mainly by MFC processes between lamprophyric magmas and the same anatectic acid end-member.

Acknowledgments

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Appendix

Set of partition coefficients employed in the computed FC process.

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Distribution coefficients from compilations of Henderson (1982), Rollinson (1993), and Sawka (1988). KF, K-feldspar; PL, plagioclase; BI, biotite; HB, amphibole; CPX, clinopyroxene; AP, apatite; TI, titanite; ZR, zircon. * estimated.

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