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THE TERTIARY EVROS VOLCANIC ROCKS (THRACE, NORTHEASTERN GREECE): PETROLOGY AND K/Ar GEOCHRONOLOGY

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Abstract: The Tertiary Evros volcanic rocks (EVR) crop out in northeastern Greece (Thrace), in close association with fault-controlled sedimentary basins, formed in an extensional regime. Three volcanic areas, called the Loutros-Feres-Dadia, Kirki-Esimi and Mesti-Petrota after the corresponding basins, could be distinguished. The rock bulk chemistry shows features of calc-alkaline to high-K calc-alkaline and, locally, shoshonitic rock series. Compositional variations indicate magmatism of convergent margins. The EVR form lava flows, domes, dykes and abundant pyroclastics. Their chemical composition ranges from basaltic andesite to rhyolite through andesite, trachyandesite, trachydacite and dacite. The basaltic andesites are two-pyroxene rocks, while the andesites are either pyroxene andesites or biotite-hornblende andesites. The trachyandesites and trachydacites have pyroxenes and biotite. The dacites mostly have biotite and hornblende and locally pyroxene. Rhyolites have mainly biotite and rarely hornblende. All the rocks are porphyritic with glassy, holocrystalline or semicrystalline textures. The K/Ar ages range from 33.4 to 19.5 Ma, establishing an Oligocene (33.4–25.4 Ma) and an Early Miocene (22.0–19.5 Ma) volcanic activity. Intercalations, however, of pyroclastic materials with Priabonian clastic sediments indicate that the volcanic activity started earlier than the Oligocene. Two main groups of rocks have been distinguished, the PxBt group comprising basaltic andesite, pyroxene andesites, trachyandesites and trachydacites, and the HblBt group comprising hornblende-biotite andesite, dacite and rhyolite. On the basis of the rock chemistry two parallel, sub-parallel or cross-cutting geochemical trends are distinguished, indicating different evolutionary histories for them. The Sr isotopic composition differs in the two groups, with Sr I.R. ranging between 0.7057 and 0.7074 in the PxBt group, and between 0.7071 and 0.7080 in the HblBt group. The PxBt group was evolved through an open system process (MFC — mixing plus fractional crystallization) in which basaltic andesite and trachydacite represent the basic and the acid end-members respectively. Although assimilation plus fractional crystallization is not excluded, MFC between a basic end-member, similar to the HblBt andesites, and an acid end-member, having rhyolitic composition, is suggested as a possible process for the evolution of the HblBt group. The parental magmas for the evolution of the PxBt group originate in an inhomogeneous and strongly metasomatized mantle through a slight modification of a primary basaltic melt. The parental magma for the evolution of the HblBt group could be a hybrid magma of the PxBt group, which evolves, under different conditions, to give the HblBt group rocks. Although the involvement of a mantle component cannot be excluded for the origin of the rhyolitic melts, partial melting of crustal material (amphibolite, basalt, andesite, gneisses, pelites, greywackes), under various P-T conditions, are responsible for the genesis of melts similar to the less evolved rhyolites.

Key words: Greece, Evros, geochemistry, petrology, volcanics, K/Ar age.

Introduction

The geology of eastern Macedonia and Thrace in northeastern Greece, is characterized by widespread Tertiary igneous rocks, both volcanic and plutonic (Fig. 1). The magmatism which produced these rocks was mostly calc-alkaline to high-K calc-alkaline in character, with subordinate shoshonitic rocks. The volcanic rocks crop out mostly in the central and eastern Hellenic Rhodope Massif (HRM) and Circum-Rhodope Belt (CRB) (Fig. 1), and continue to the north into Bulgarian territory (Yanev et al. 1998 and references therein).

The volcanic products are associated with the intensive Tertiary volcanic activity affected the Balkan Peninsula, and are regarded as the result of the underthrusting of the African plate below the southern European margin. Although the evolution of the volcanism has been reconstructed in detail in the central Aegean Sea (Innocenti et al. 1982; Fytikas et al. 1985; Pe-Piper 1994), it has only partly been investigated (Innocenti et al. 1984; Eleftheriadis 1995; Christofides et al. 2001) in northeastern Greece.

Here, new petrological, geochemical, and geochronological (K/Ar) data are presented for the Evros volcanic rocks (EVR) in Thrace, and general aspects of their origin and evolution are

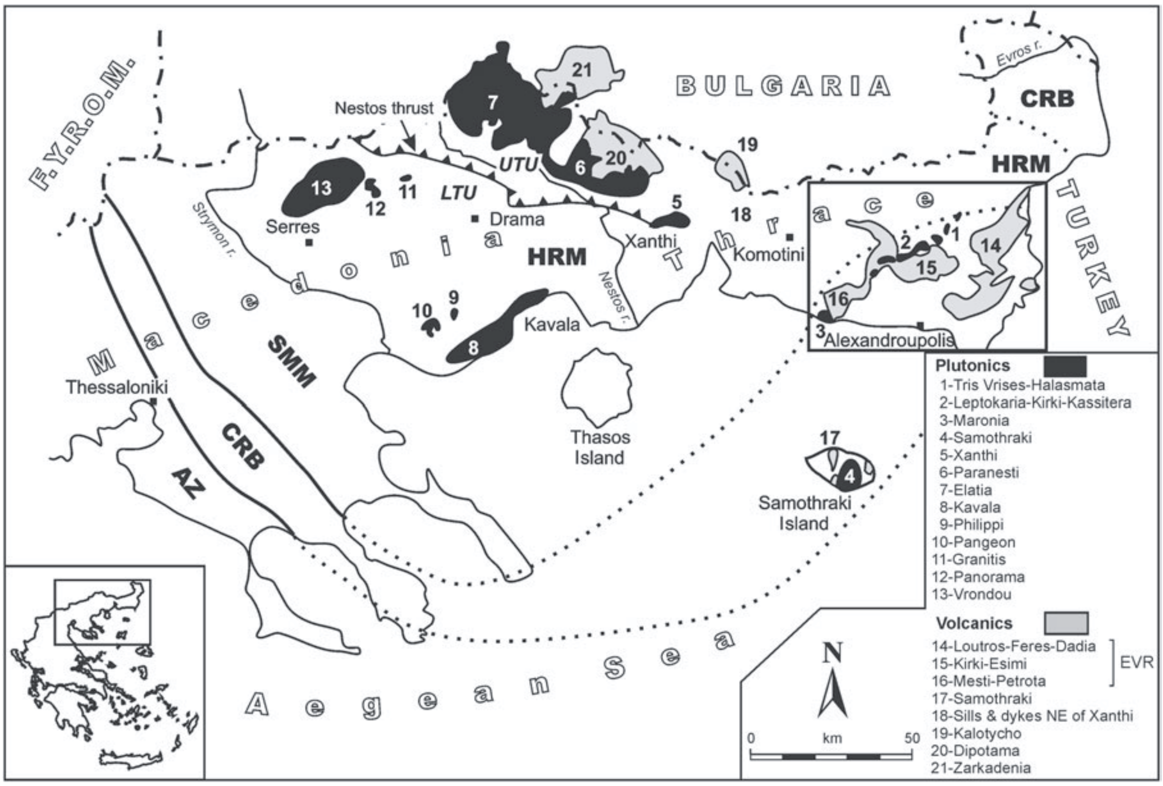

Fig. 1. Geological sketch map of the central eastern Hellenic Hinterland. **AZ** — Axios (Vardar) Zone; **CRB** — Circum-Rhodope Belt; **SMM** — Serbo-Macedonian Massif; **HRM** — Hellenic Rhodope Massif; **UTU** — Upper Tectonic Unit; **LTU** — Lower Tectonic Unit. Plutonic and volcanic outcrops are shown. **EVR** — Evros volcanic rocks. **F.Y.R.O.M.** — Former Yougoslavian Republic of Macedonia.

considered, aiming at the understanding of the volcanic history of the area.

Geological setting

The EVR, which are named after Evros River (Fig. 1) and the Evros County, crop out in the eastern parts of the HRM and CRB in Thrace. The HRM is a polymetamorphic terrain that extends along the Greek-Bulgarian borders and covers eastern Macedonia and Thrace in Greece, and southern Bulgaria. The HRM is situated between the Balkan belt to the north and the Dinarides-Hellenides to the south-southwest. It is bounded to the west by the Serbo-Macedonian Massif (SMM), a structurally complex domain of predominantly high-grade metamorphic rocks and numerous granitoids mainly of Jurassic and Tertiary age. The HRM and SMM are now regarded as a "single major element of the Tethyan orogenic system" (Burg et al. 1995) formed through deep level subduction–accretion processes acting on Paleozoic-Mesozoic precursors (Barr et al. 1999). The interpretation of Rhodope as a fragment of pre-Alpine age (possibly of Hercynian or Precambrian) is rejected (Ricou et al. 1998).

The CRB comprises a Late Paleozoic and Mesozoic marginal volcano-sedimentary narrow belt consisting of phyllites, schists, crystalline limestones and marbles (Kauffman et al. 1976; Kockel et al. 1977; De Wet et al. 1989; Ioannidis 1998), bordering both the HRM to the southeast and the SMM to the west (Fig. 1). It was subjected to a Late Jurassic–Early Cretaceous low-grade metamorphism associated with the main CRB foliation, subparallel to the bedding (Vergely 1984). Ricou et al. (1998) reject the concept of a Mesozoic CRB as a stratigraphic Rhodope cover. Instead they support the idea of a two-fold classification as roof greenschists (Alexandroupolis and Mandrica schists roofing the eastern Rhodope) and the western greenschists (Mesozoic Chalkidiki sediments).

Major thrust zones separate HRM into distinct geological units. On the basis of geological and petrological criteria, the western and central HRM is distinguished into an Upper Tectonic Unit (UTU) or Sideronero Unit and a Lower Tectonic Unit (LTU) or Pangeon Unit (Papanikolaou & Panagopoulos 1981; Mposkos 1989; Kilias & Mountrakis 1990), separated by an approximately SSE–NNW striking thrust plane, the Nestos thrust.

The metamorphic basement of the HRM is made up of schists, gneisses and amphibolites, marbles and ultramafic rocks. Its metamorphic history is rather complicated and is characterized by an ultra high pressure metamorphism (Mposkos et al. 2001; Liati et al. 2002), an eclogite-facies metamorphism, subsequently overprinted in the amphibolite-facies metamorphism, followed by a greenschist-facies metamorphism (Liati & Seidel 1996 and references therein). The HRM was not metamorphosed as a single geotectonic element but rather consisted of different fragments subducted and exhumed at different times (Liati et al. 2002). The metamorphism in eastern Rhodope is significantly older (ca. 74 Ma) than in the

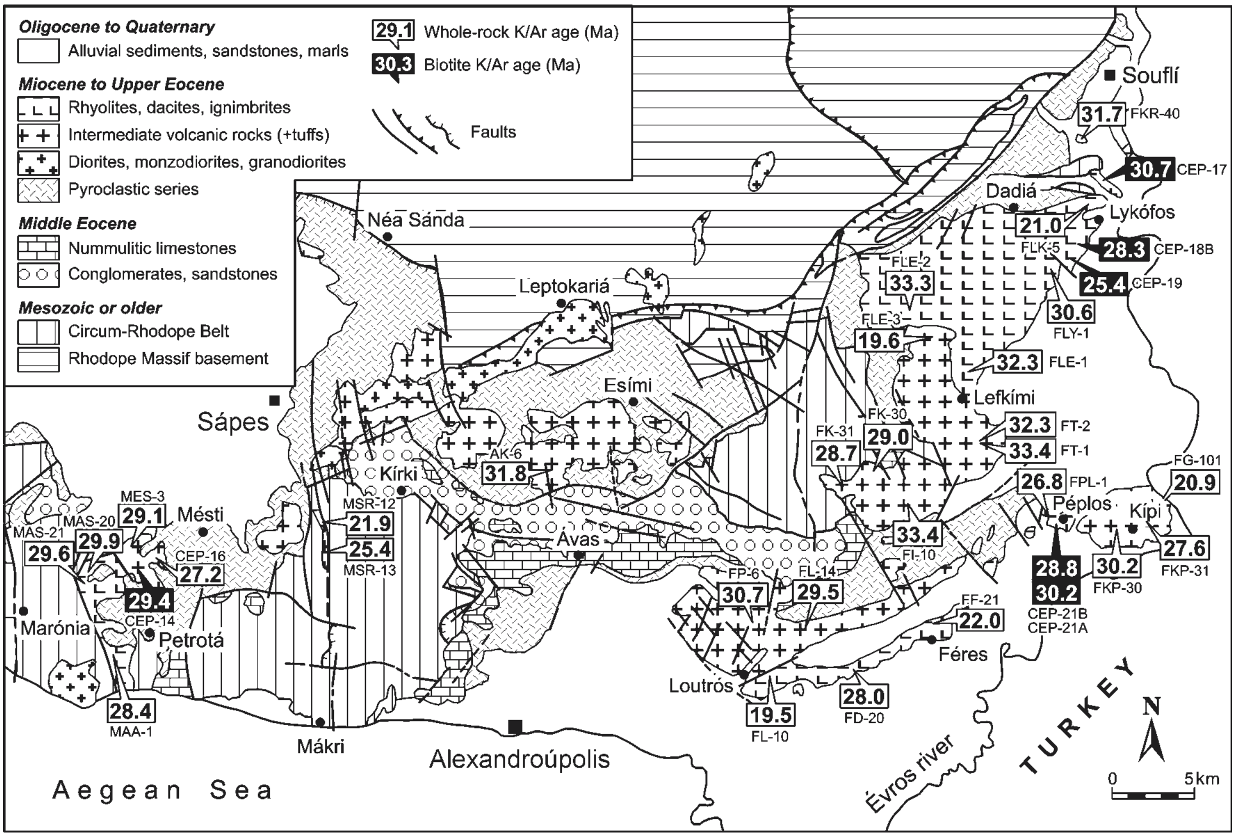

Fig. 2. Geological map of the Evros volcanic rocks. K/Ar ages are shown.

central part of it. The metamorphic basement of the HRM, particularly the eastern part, and CRB is covered by a clastic Lutetian sequence consisting of basal conglomerates, sandstones and nummulitic limestones.

A characteristic feature of the Tertiary evolution of the HRM and the CRB is the presence, at their margins and on them, of fault-controlled (depression) sedimentary basins, formed under tensional tectonics, following an intense Eocene orogenic phase, which affected all the Inner Hellenides. The formation of the basins, with which the Tertiary magmatism is associated, started in the Middle Eocene (Lutetian) and lasted up to the Pliocene. The Evros area contains three large basins, Maronia-Petrota, Kirki-Esimi and Feres-Soufli-Dadia (Fig. 2), as well as a number of smaller basins (Papadopoulos 1979, 1980, 1982).

The change of the paleogeographical conditions, in the various basins, started in the Late Eocene. The environment in the Maronia-Petrota Basin was transitional and sub-aerial, and the deposition of volcanic products continued right through the Oligocene (Innocenti et al. 1984). The volcanic products comprise a series consisting of pyroclastic layers with intercalations, at its basal part, of conglomeratic layers composed of volcanic elements associated locally with lahars. In the upper part of the series, lava flows predominate, overlying an ignimbritic sequence (Frass et al. 1990).

In the Kirki-Esimi Basin, strong subsidence conditions persist, with deposition of volcano-sedimentary products (marly sandstones and claystones of Priabonian age dominate), followed in places by intercalations of volcanic products, represented mainly by lava flows, domes, associated with rare volcanic agglomerates (Innocenti et al. 1984).

The Feres-Soufli-Dadia Basin is the widest and the most affected by subsidence. Its geology comprises a Lutetian basal clastic sequence, Priabonian sandstones, marls, and conglomerates, and an Oligocene sequence of marly and clayey sediments. The volcanic products, mostly sub-aqueous and subaereal pyroclastic deposits, are intercalated in the Priabonian and Oligocene sequence. Several ignimbritic units are seen in the Oligocene sequence as well as lava flows, domes and dykes.

Tertiary magmatic activity

The volcanic rocks are widespread in northeastern Greece particularly in eastern Macedonia and Thrace (Fig. 1). Two major volcanic provinces have been defined, one north of Xanthi town, known as the Kalotycho volcanics (Eleftheriadis & Lippold 1984; Innocenti et al. 1984; Eleftheriadis 1995), and one in western Thrace, known as the Evros volcanic rocks (EVR) (Rentzeperis 1956; Sideris 1973; Eleftheriadis et al. 1989; Frass et al. 1990; Karafoti & Arikas 1990; Arikas & Voudouris 1998; Christofides et al. 2001).

According to geochronological and stratigraphic data the volcanism in the area started in Middle Eocene times producing abundant pyroclastics and ignimbrites, although a few andesitic products with supposed Priabonian age, crop out in Feres-Dadia area (Skarpelis et al. 1987). The volcanic activity culminated during the Late Oligocene (Innocenti et al. 1984) with eruption of high-K calc-alkaline to shoshonitic volcanics of mostly intermediate composition. Pyroclastics, interlayered with Oligocene sediments, rhyolitic ignimbrites a few hundreds meters thick, breccias, lava flows, dykes and domes of basaltic andesite to rhyolite composition are also present. Volcanism ended in the Miocene with both acid and intermediate volcanic products (Eleftheriadis et al. 1994; Innocenti et al. 1994; Vlahou et al. 2001).

The volcanism of northeastern Greece, including the EVR, was developed after the thickening/uplift of the Hellenic Orogen and its subsequent extensional collapse. It shows a "bimodal" character, in the sense that intermediate (andesitic) and acid (rhyolitic) compositions dominate while compositions in between them (latitic) are restricted. This bimodal character is atypical for convergent plate margins but common for magmatism related to lithospheric delamination or continental rifting (Yanev et al. 1998). If the volcanic products in the Bulgarian Rhodope Massif (Harkovska et al. 1989) and the Aegean volcanism (Fytikas et al. 1985) are considered, it is obvious that there is a southward migration of the volcanic activity.

Pamić et al. (2002 and references therein) reviewing the geophysical, geological, petrological and geochemical data of the Late Paleogene magmatic associations of the Periadriatic–Sava–Vardar Magmatic Belt (PSVMB), including the Hellenides, support the view that the geodynamic evolution of these magmatic associations was related to the Africa-Eurasia Suture Zone, which was dominated by break-off of the subducted lithospheric slab of the Mesozoic oceanic crust, at depths of 90–100 km.

Petrography

The EVR comprise intermediate and acid rocks (Fig. 2), which have been classified according to the TAS (Total Alkali vs. Silica) diagram of Le Maitre (1989) as basaltic andesites, andesites, trachyandesites, dacites, trachydacites, and rhyolites (Fig. 3). The trachyandesites are further subdivided into latites (5 samples) and benmoreites (2 samples) according to Na_2O and K_2O contents. Here, we use the general term trachyandesites. For simplicity three volcanic areas could be distinguished (Fig. 2): **a** — Loutros-Feres-Dadia, **b** — Kirki-Esimi, **c** — Mesti-Petrota, corresponding to the host depression basins. In each area both intermediate and acid lavas are present in association with pyroclastics. In the northeastern and southwestern parts of the Loutros-Feres-Dadia area the acid rocks, mostly rhyolites, dominate while in the middle part andesite and to a lesser extent dacite are the prevailing rock-types. Lava flows and domes, in some cases exhibiting columnar jointing (Fig. 4a), are very often associated with pyroclastics. The latter, in most cases, are intruded or covered by the former. In the Kirki-Esimi area the most widespread rock is andesite, often with columnar jointing. Rhyolites are present in the form of a dense net of NW–SE trending dykes in the northeastern part of the area. The overall width of the dykes varies from a few tens of centimeters to hundreds of meters whereas their length extends from tens of meters to some kilometers. Dacites occur mostly in the eastern part of it, west of Esimi village. In the Mesti-Petrota area, andesite is again the prevailing rock followed by dacite and rhyolite.

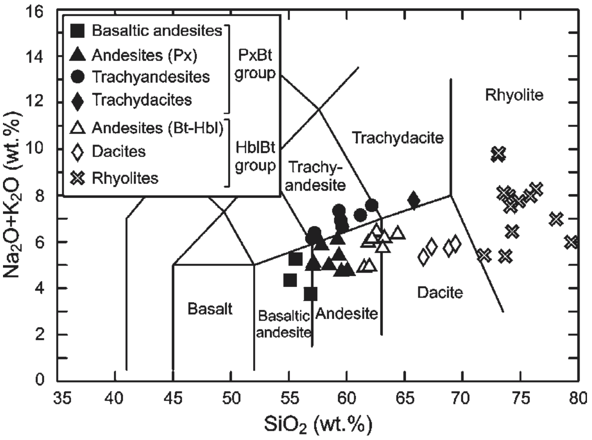

Fig. 3. Total alkali vs. silica (TAS) classification of the Evros volcanic rocks (after Le Maitre 1989).

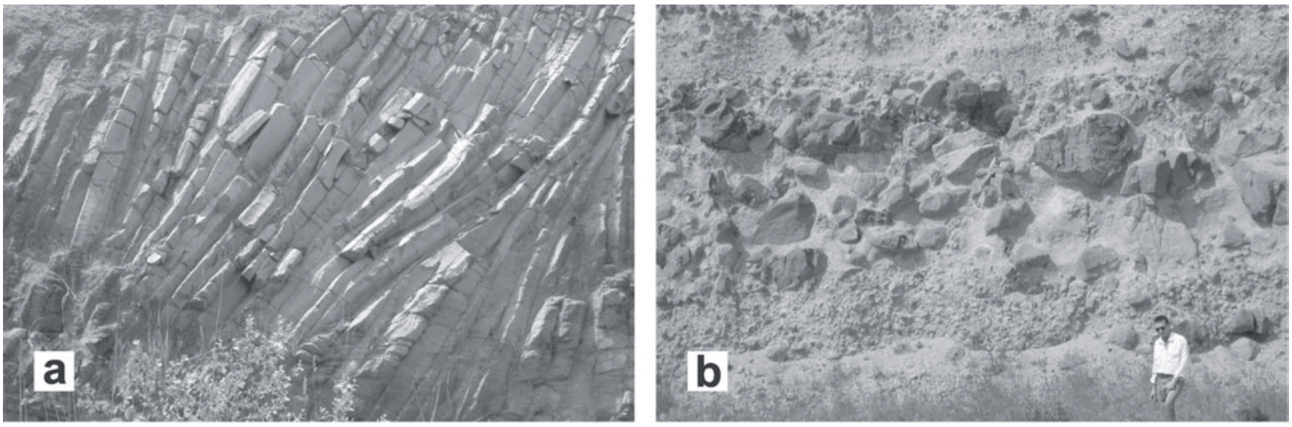

Fig. 4. **a** — Columnar jointing in rhyolites from Loutros-Feres-Dadia area. **b** — Lahar from Mesti area.

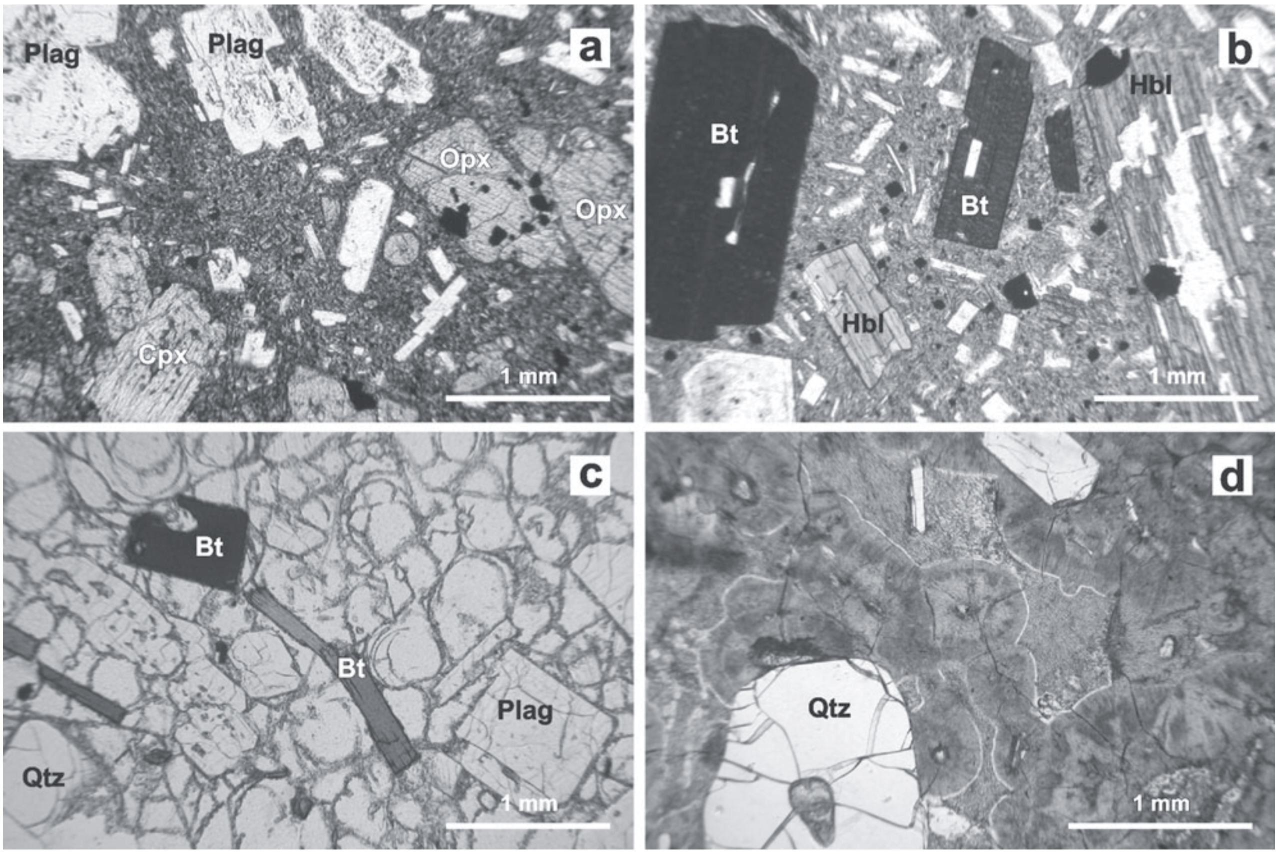

Fig. 5. Microphotographs from the Evros volcanic rocks. **a** — Pyroxene andesite (crossed Nicols); **b** — Hornblende-biotite andesite (crossed Nicols); **c** — Rhyolite with perlitic texture (parallel Nicols); **d** — Rhyolite with sphaerolitic texture (parallel Nicols).

Rhyolitic ignimbrites, strongly welded, tuffs and lahars (Fig. 4b) are widespread.

All rocks show porphyritic texture with groundmass ranging between 40 and 80 wt. %. Phenocrysts are more abundant (20 to 60 wt. %) in basaltic andesites and andesites than in dacites and rhyolites (30 to 50 wt. %). Basaltic andesites contain mainly plagioclase (An_{90}–An_{50}) and clino- and orthopyroxene phenocrysts, set in a semicrystalline to hollocrystalline groundmass (Fig. 5a). Andesites are distinguished into two groups namely the pyroxene andesites and the biotite-hornblende andesites (Fig. 5b). Hornblende-biotite andesites are found mainly in the Kirki-Esimi and Loutros-Feres-Dadia areas. Trachyandesites and trachydacites have pyroxenes and biotite. Dacites and rhyolites consist of plagioclase (An_{60}–An_{20}), sanidine (Or_{75-65}), quartz, biotite and subordinate hornblende set in a glassy or semiglassy matrix, which very often exhibits very nice perlitic and sphaerolitic textures (Fig. 5c,d). Apatite, titanite and zircon are accessories in all rocks. More information on the petrography and geology of the EVR can be found in Rentzeperis (1956).

Two groups of rocks could be distinguished, on the basis of their mineralogy. The first group consists of the basaltic andesites, the pyroxene andesites, the trachyandesites and the trachydacites and it will be hereafter referred to as the PxBt group since it is characterized by the presence of pyroxenes ± biotite. The second group comprises the biotite-hornblende andesites, the dacites and the rhyolites, and will be referred to as the HblBt group.

Analytical techniques

The rock analyses were performed by XRF following Brown's et al. (1973) method. Pressed pellets were used. The operating conditions were 60 kV and 40 mA. A Cr tube was used for major elements, a Rh tube for Nb, Zr, Y, Sr and Rb, and a Au tube for the other trace elements.

Minerals were analysed by Energy Dispersive Spectrometry (EDS) at the laboratory of Electron Microscopy, University of Thessaloniki, Greece. Mineral phases were imaged with back-scattered electrons (BSE) and quantitatively analysed using a LINK AN 1000 EDS microanalyser attached to a JEOL JSM-840 Scanning Electron Microscope. The operating conditions were 15 kV accelerating potential, beam current 3 nA, surface electron beam 1 μm^2 and counting time 80 seconds. The ZAF-4/FLS software provided by LINK was used for corrections. Minerals (albite, orthoclase, diopside, wollastonite, olivine, periclase) and pure metals were used as standards.

K/Ar age determinations were performed at the ATOMKI Institute for Nuclear Research of the Hungarian Academy of Sciences, Debrecen. Both whole rock (lavas and a few tuffs) and biotite separates were analysed.

Representative rock samples of about 1 kg each were collected, on the basis of their freshness and purity. After crushing, approximately 20 g of the 300–200 μm size fraction was taken, washed and oven dried. A portion of it was ground in an agate mortar and used for potassium analysis. Powdered samples were treated with a mixture of acids (HF, HNO_3 and H_2SO_4) in teflon beakers and finally dissolved in 0.2 M HCl. The potassium analysis was carried out by flame photometry with a Na buffer and Li internal standard. Multiple runs of inter-laboratory standards (Asia 1/65, LP-6, HD-B1) indicated the accuracy and reproducibility to be within 2–3 %.

For argon analysis the samples were wrapped in aluminium foil and copper sieve, preheated for about 24 h at 150–200 °C in a vacuum. The argon was extracted at about 1500 °C in Mo crucibles, in a previously backed stainless steel vacuum system. Reactive gases were purified by Ti and SAES getters and liquid nitrogen traps. Argon was analysed using an isotope dilution method (^{38}Ar spike was added from gas pipette system) in a 15 cm radius sector-type mass spectrometer, used in static mode, with a single collector system designed and constructed by Balogh (1985), at the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary. Carefully checking of mass discrimination of the mass spectrometer is routinely carried out with atmospheric argon before the samples are run in the mass spectrometer. Details of the instruments, the applied methods and results of calibration have been described elsewhere (Balogh 1985).

Atomic constants suggested by Steiger & Jäger (1977) were used for calculating the ages. All analytical errors represent one standard deviation (i.e. 68 % analytical confidence level). Since we base our analytical errors on the long term stability of instruments and on the deviation of our results obtained on standard samples from the interlaboratory mean the analytical errors are likely to be overestimated.

K/Ar geochronology

The K/Ar ages obtained range from 33.4 to 19.5 Ma (Fig. 2; Table 1), which enabled us to broadly distinquish two periods of volcanic activity: a) in the Oligocene (33.4–25.4 Ma) and b) in the Early Miocene (22.0–19.5 Ma). K/Ar ages reported by Innocenti et al. (1984), range between 33 and 24 Ma. Miocene ages are reported for the first time for the EVR. However, volcanic activity of this age is documented by K/Ar and Rb/Sr dating on both whole rock and minerals on Samothraki Island (Fig. 1) (Eleftheriadis et al. 1994; Vlahou et al. 2001) and on Limnos Island (Innocenti et al. 1994) in the northern

Table 1: K/Ar dating of selected samples from the Evros volcanic rocks.

Sample	Rock-type	Area*	SiO_2 (wt.%)	Dated fraction**	K%	^{40}Ar rad %	^{40}Ar rad (ccSTP/g) × 10^{-6}	K/Ar age (Ma)	± Error
FLE3	Basaltic andesite	LFD	53.87	w.r.	0.80	45.0	0.613	19.60	0.86
FKR40	Basaltic andesite	LFD	54.98	w.r.	1.01	64.4	1.259	31.66	1.26
MES3	Basaltic andesite	MP	55.77	w.r.	1.44	59.2	1.320	29.12	1.18
FG101	Andesite (Px)	LFD	55.53	w.r.	1.73	37.4	1.415	20.92	1.00
FKP30	Andesite (Px)	LFD	57.49	w.r.	2.13	38.5	2.517	30.15	1.42
MAA1	Andesite (Px)	MP	57.90	w.r.	1.75	76.3	1.948	28.39	1.09
MSR12	Andesite (Px)	KE	58.61	w.r.	1.59	42.6	1.365	21.92	0.99
CEP16	Andesite (Px)	MP	58.90	w.r.	1.81	47.7	1.926	27.20	1.17
FK31	Andesite (Bt-Hbl)	LFD	60.40	w.r.	2.52	79.5	2.837	28.73	1.10
MSR13	Andesite (Bt-Hbl)	KE	60.73	w.r.	1.64	36.7	1.628	25.42	1.22
FT2	Andesite (Bt-Hbl)	LFD	61.16	w.r.	2.09	75.6	2.646	32.29	1.24
AK6	Andesite (Bt-Hbl)	KE	62.25	w.r.	1.74	72.7	2.171	31.83	1.23
FKP31	Trachyandesite	LFD	55.12	w.r.	2.89	73.2	3.124	27.58	1.07
FP6	Trachyandesite	LFD	58.18	w.r.	1.84	68.1	2.208	30.68	1.20
FL14	Trachyandesite	LFD	59.99	w.r.	2.26	73.2	2.612	29.46	1.14
MAS20	Trachydacite	MP	63.81	w.r.	4.26	77.3	4.988	29.89	1.15
MAS21	Trachydacite	MP	64.10	w.r.	4.31	85.3	5.006	29.61	1.12
FI10	Dacite	LFD	65.70	w.r.	2.00	39.5	2.624	33.40	1.55
FK30	Dacite	LFD	66.79	w.r.	1.92	36.0	2.182	29.00	1.42
FLE1	Dacite	LFD	68.23	w.r.	2.39	81.1	3.026	32.28	1.23
FT1	Dacite	LFD	68.79	w.r.	1.94	59.1	2.540	33.35	1.35
CEP14	Dacite	MP		Bt	6.05	89.2	6.984	29.44	1.11
FLK5	Rhyolite	LFD	69.22	w.r.	3.06	71.8	2.511	20.99	0.82
FPL1	Rhyolite	LFD	71.09	w.r.	3.49	69.1	3.657	26.77	1.05
FF21	Rhyolite	LFD	71.36	w.r.	3.72	71.7	3.197	21.96	0.85
FLE2	Rhyolite	LFD	71.54	w.r.	2.16	55.9	2.824	33.26	1.36
FL10	Rhyolite	LFD	71.69	w.r.	6.85	77.5	5.228	19.53	0.75
FD20	Rhyolite	LFD	72.16	w.r.	3.69	74.2	4.043	27.98	1.08
FLY1	Rhyolite	LFD	79.09	w.r.	2.71	43.3	3.248	30.58	1.37
CEP17	Rhyolite	LFD		Bt	6.65	87.1	8.009	30.70	1.16
CEP18B	Rhyolite	LFD		Bt	7.03	41.1	7.800	28.30	1.29
CEP19	Rhyolite	LFD		Bt	7.23	69.9	7.182	25.37	0.99
CEP21A	Rhyolite	LFD		Bt	6.36	87.3	7.525	30.16	1.14
CEP21B	Rhyolite	LFD		Bt	6.32	86.3	7.122	28.77	1.09

* LFD — Loutros-Feres-Dadia; KE — Kirki-Esimi; MP — Mesti-Petrota. ** w.r. — whole-rock; Bt — biotite

Aegean Sea. The products of the Oligocene volcanism are much more widespread than those of the Miocene. However, more, shorter, periods of activity could be distinguished, if details of the stratigraphy and the spatial distribution of the volcanic products are taken into account. Moreover, intercalations of pyroclastic materials with Priabonian clastic sediments indicate that the volcanic activity started earlier than the Oligocene, possibly in the Middle Eocene.

Within a single volcanic area (basin), the maximum difference in age (w.r.) is observed in the Loutros-Feres-Dadia area, where the age of the intermediate and acid rocks ranges between 32 and 20 Ma and 33 and 20 Ma respectively. In the Kirki-Esimi area, the age of the intermediate rocks (no data are available for the acid rocks) ranges between 32 and 22 Ma, and in the Mesti-Petrota area between 29 and 27 Ma. In the last area the age of the acid rocks is about 30 Ma. It is obvious, according to the available data, that the volcanic activity continued up to the Miocene with the most recent volcanic products limited to the Loutros-Feres-Dadia area. A temporal gap of about 3 Ma has been noticed between the Oligocene and the Miocene volcanic activity.

“Bimodality” is present in each volcanic period, with repeated acid and intermediate phases having, in general, similar ages. Compared with the east Rhodope volcanism in Bulgaria (Yanev et al. 1998) the Evros volcanism seems to follow it. However, in the Evros area the volcanic activity continues up to the Early Miocene. Moreover, it culminated during the Late Oligocene.

Geochemistry

The analysed EVR have a wide spectrum of silica content, ranging from 54 to 79 wt. % (Table 2). They show features of orogenic volcanic rocks, such as the absence of Fe enrichment, the low TiO_2 content (<0.90 wt. %), and the K_2O/Na_2O ratios, which is close to unity for many silicic rocks. Their bulk chemical compositions indicate affinities of calc-alkaline to high-K calc-alkaline and shoshonite series (Fig. 6), characteristic of subduction related rock series (Wilson 1989).

The two groups of rocks, namely PxBt and HblBt, mentioned in the Petrography section, clearly define two separated geochemical trends, which could be distinguished on various variation diagrams such as on the K_2O, P_2O_5 and MgO diagrams (Fig. 7). In the PxBt group, two samples from the Maronia area, showing shoshonite composition, deviate from the general potash trend. In the variation diagrams all major elements, except K_2O, decrease with increasing silica content in both groups. P_2O_5 behaviour is different in the two groups, increasing in the PxBt and decreasing in the HblBt group. In Fig. 8 the compositional variations of selected trace elements are shown. The distinction of the analysed rocks into the two above mentioned trends is obvious also in nearly all trace element diagrams. Rb, Ba, Ce and Nd increase with silica in both groups, although the last two show some scatter in the HblBt group. Sr and Zr increase in the PxBt group and decreases (Sr) or remains constant (Zr) in the HblBt group. Cu and V decrease in both groups. Y decreases in the PxBt group and is

Table 2: Major and trace element XRF analyses of selected samples from the Evros volcanic rocks.

Rock-type	Basaltic andesite	Andesite (Px)	Trachy-andesite	Trachy-dacite	Andesite (Hbl-Bt)	Dacite	Rhyolite
Sample	FLE3	FG101	FG100	MAS20	AK3	FT1	FD20
SiO_2 (wt.%)	53.87	55.53	56.68	63.81	61.27	68.79	72.16
TiO_2	0.81	0.90	0.79	0.49	0.49	0.55	0.28
Al_2O_3	16.83	17.65	17.67	14.62	16.03	15.05	13.41
Fe_2O_3	8.00	7.75	7.00	4.15	5.44	2.32	1.64
MnO	0.10	0.11	0.10	0.09	0.05	0.02	0.02
MgO	4.76	1.77	2.22	2.08	3.53	1.59	0.98
CaO	8.97	8.35	8.04	3.99	4.74	4.82	2.32
Na_2O	3.26	2.84	3.40	2.27	4.08	3.48	1.63
K_2O	0.99	2.10	2.93	5.29	2.19	2.38	4.63
P_2O_5	0.17	0.20	0.24	0.25	0.14	0.14	0.07
LOI	2.19	2.91	0.92	2.47	1.72	0.66	2.95
Total	99.95	100.11	99.99	99.51	99.68	99.80	100.09
Nb (ppm)	5	7	7	11	5	6	11
Zr	146	187	193	194	134	145	146
Y	26	29	27	21	20	26	27
Sr	390	487	489	454	296	314	327
Rb	83	184	112	214	80	80	168
Zn	114	117	101	79	89	63	57
Cu	68	38	42	25	16	14	5
Ni	33	14	12	20	6	7	2
Cr	92	47	41	44	35	33	23
Ce	79	88	91	65	81	105	130
Nd	24	34	25	36	15	26	24
V	166	154	126	94	83	71	18
La	27	41	45	79	36	70	82
Ba	595	534	507	995	470	572	430
Sc	36	23	19	13	16	13	7

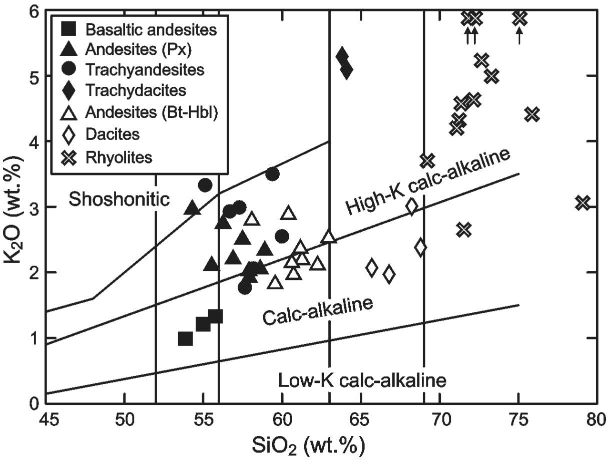

Fig. 6. K_2O vs. SiO_2 classification of the Evros volcanic rocks (after Peccerillo & Taylor 1976).

scattered in the HblBt group, while Cr is scattered in the PxBt group and decreases in the HblBt group. The two trends, which have been defined by the PxBt and the HblBt group respectively, are confirmed by some element–element diagrams, on which they are much more distinct (Fig. 9). It must be noticed here that rhyolites, which show quite extensive internal variability, could be regarded as establishing a separate group. The same is not valid for dacites, although in CaO and TiO_2 vs. SiO_2 diagrams they deviate from the andesite-rhyolite trend.

Selected MORB-normalized multi-element patterns of the investigated rocks are shown in Fig. 10. In each group the patterns are similar exhibiting strong depletion in the HFSE relative to LILE (large ion lithophile elements), with distinct negative Nb, P and Ti anomalies, indicative of convergent plate margin magmatism.

The two groups have different Sr isotopic compositions. The PxBt group has lower Sr I.R., than the HblBt group. In

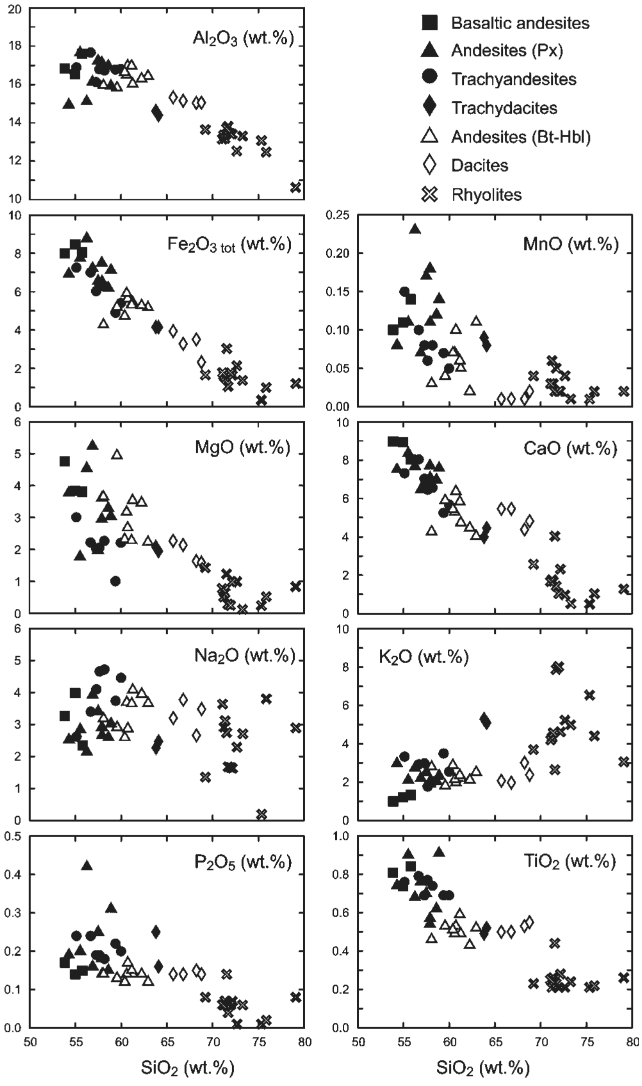

Fig. 7. Major element variation Harker diagrams for the Evros volcanic rocks.

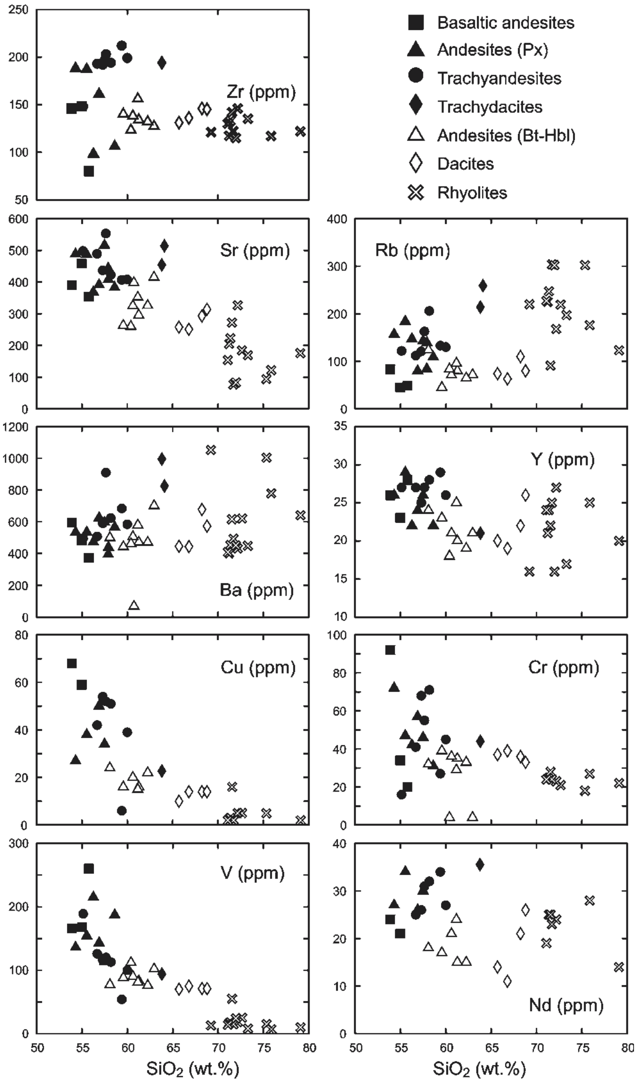

Fig. 8. Trace element variation diagrams for the Evros volcanic rocks.

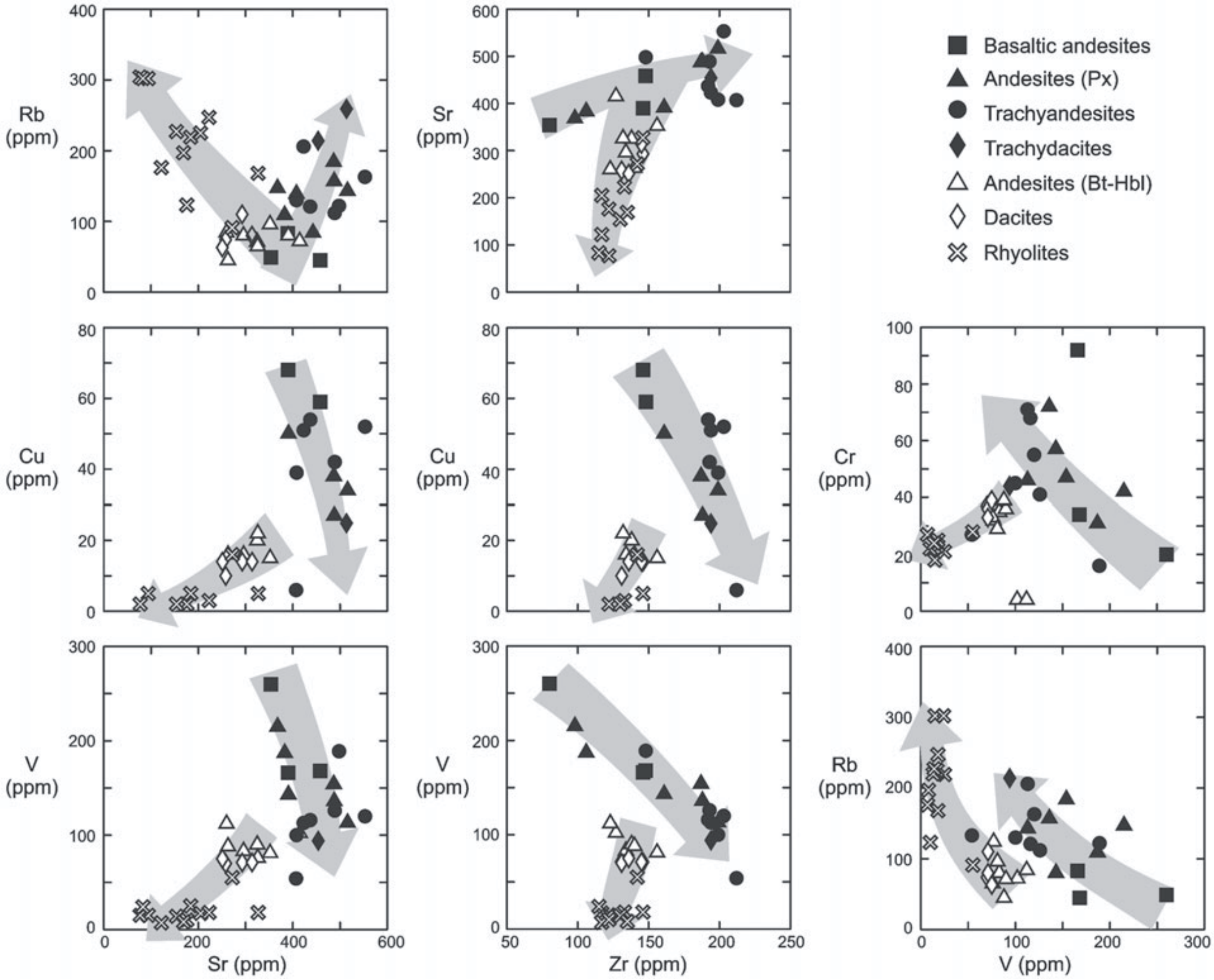

Fig. 9. Inter-element variation diagrams for the Evros volcanic rocks. Trends are shown by shaded arrows.

both groups the Sr I.R. increases with silica, ranging between 0.7057 and 0.7074, and between 0.7071 and 0.7080 in the PxBt and the HblBt group respectively.

Discussion

Mineralogy, major and trace element geochemistry, and Sr isotope composition of the rocks investigated, tend to support the following: i) the existence of two distinct rock groups, the PxBt and the HblBt, which have different evolutionary paths, ii) basaltic andesites, pyroxene andesites, trachyandesites and trachydacites constitute the first group while the second group comprises biotite-hornblende andesites, dacites and rhyolites. iii) the members of each group are the results of a single evolutionary process, iv) the existence of an evolutionary relationship between the two groups is ruled out as indicated by the parallel, sub-parallel or cross-cutting trends of various elements of them.

The isotopic composition of each group favours an open rather than a closed system process. In particular the PxBt group could be the result of a mixing or an MFC (mixing plus fractional crystallization) process with high *r* (rate of mixing or assimilation/rate of crystallization) value, in which the basaltic andesites represent the basic end-member, while the acid end-member is represented either by the trachydacites or by a composition close to it. The shoshonitic rocks are excluded from the above procedure. Their origin and evolution is not discussed here due to the limited data available. However, the origin of similar potassic rocks, reported by Soldatos et al. (1998) from Vrondou (NE Greece) was ascribed to partial melting of an enriched mantle wedge under different conditions of pressure and/or composition. On the other hand an AFC (assimilation plus fractional crystallization) is ruled out since a fractionation process with low *r*, controlled mainly by plagioclase accumulation, would result in decreasing of Sr towards the more evolved rocks. The behaviour of MgO, Fe_2O_{3tot}, CaO, Y and V implies the involvement of clinopyroxene and/or hornblende as residual phases. However, taking into account that Al_2O_3 remains generally constant and that hornblende is absent from the liquid phase it seems more probable that clinopyroxene, among the mafic minerals, has played an important role during fractionation.

Before going on to discuss the evolution of the HblBt group, it is worth noting that the extensive outcrop of the rhyolitic rocks argues against the genesis of the rhyolitic magma

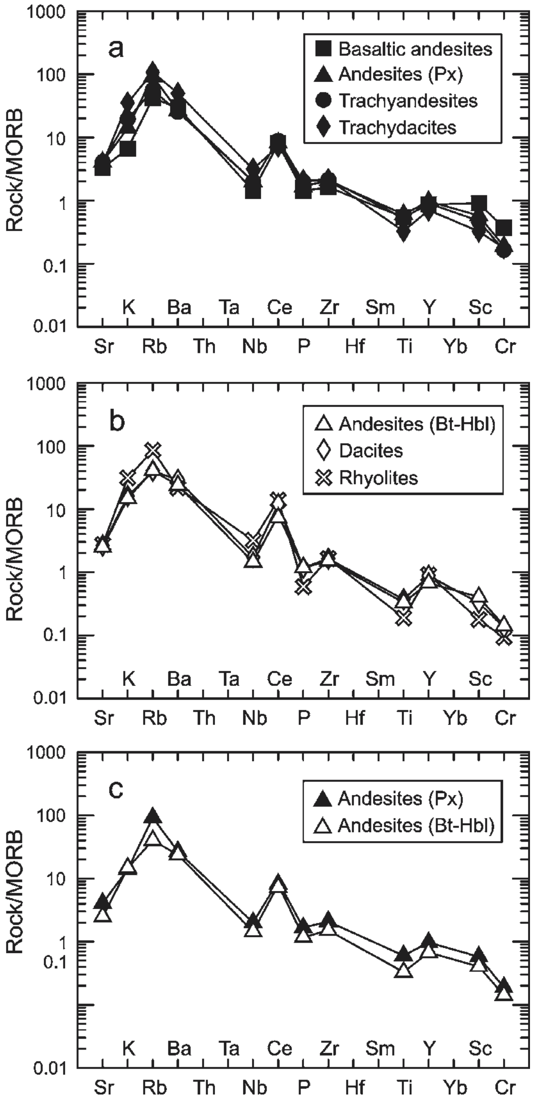

Fig. 10. MORB-normalized spider diagrams (normalization after Pearce 1983) of selected samples from the Evros volcanic rocks. **a** — PxBt group; **b** — HblBt group; **c** — comparison of andesites of the two groups.

through a simple fractional crystallization of an andesitic magma. Rather it favours the existence of an anatectic rhyolitic magma, which could be the acid end-member mixed with a basic end-member, having composition similar to that of the HblBt andesites, through a possible MFC process to give the HblBt group including the less acid rhyolites. This means that some of the rhyolites are hybrid rocks. On the other hand the absence of mingling phenomena argues in favour of an AFC process.

Following the previous discussion the parental magmas for the evolution of the PxBt group are the basaltic andesite and the trachydacite (Fig. 3) or a similar magma. The relatively low values of Sr isotopes, the low silica content and the spider diagram patterns of the basaltic andesite show genesis from an enriched mantle. The precursor of the basaltic andesite magmas could probably be a basaltic magma, which underplated crust, became contaminated and underwent high pressure fractionation (olivine, pyroxene). Fractionation took place at the base of the crust since primary magmas usually do not reach the earth's surface in environments with thick continental crust due to their density. This explains the comparative rarity of basaltic lavas in continental margin arcs (Wilson 1989). The trachydacite magma could not be the result of crustal melting since its composition does not fit the field of any experimental crustal melts (Fig. 11). Its high LILE content and its relatively high Sr isotopes suggest an origin by partial melting of a strongly metasomatized mantle. This means that the mantle in the area was inhomogeneous, which has been reported by many authors (e.g. Christofides et al. 1998; Pe-Piper et al. 1998). Moreover, in the Maronia area monzonitic rocks having high LILE values, outcrop (Papadopoulou et al. 2001).

For the HblBt group evolution hornblende-biotite andesites and rhyolites (Fig. 3) are regarded as the parental magmas. The latter is regarded as the parental magma if the evolution process is MFC. The hornblende-biotite andesites could also be genetically related to an inhomogenous metasomatized mantle by the same procedure as discussed above for the PxBt group. Its Sr isotope composition precludes a common origin with the basaltic andesite since melting of the same mantle under different degree of melting would give melts with the same isotope composition. The starting point (hornblende-biotite andesites) of the trend of this group is nearly always found on the PxBt evolution line (Figs. 7, 8, 9). Taking this into account and the similar spider diagram patterns of the two types of andesites, the parental magma of the hornblende-biotite andesite could be a hybrid magma of the PxBt group, which evolves, under different conditions (e.g. higher P_{H_20}) to give the HblBt group rocks.

The Sr isotopic composition of the rhyolites (I.R. ranges from 0.7069 to 0.7080) does not exclude an origin by partial melting of an enriched mantle. Moreover, it is widely accepted that such an inhomogeneous and enriched mantle exists in the broader area. On the other hand, for the genesis of such rhyolitic melts, extremely large masses of this mantle, under a very low degree of melting are needed. Hence, the origin of

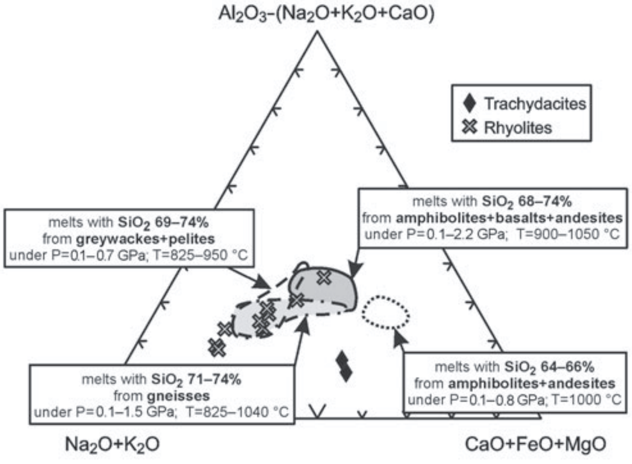

Fig. 11. Plot of the trachydacites and rhyolites on the Al_2O_3–(Na_2O+K_2O+CaO)–Na_2O+K_2O–CaO+FeO+MgO diagram. Shaded areas represent experimental melts. See text for explanation.

the rhyolitic melts, at least the more acid ones, could be related to partial melting of crustal rocks.

In the Rhodope Massif and the broader area crustal rocks having silica contents greater than 60 % exist, the Sr isotopic ratios of which ranges between 0.7066 and 0.7372 (recalculated from Soldatos et al. (2001) on the basis of 30 Ma). Numerous melting experiments are reported in the literature, which have been carried out on rocks representing the composition of the crust (tonalites, gneisses, basalts, andesites, amphibolites, pelites, greywackes) under various P-T conditions, and which have produced melts with variable SiO_2 content. These experimental melts plot on the diagram Al_2O_3–(Na_2O+K_2O+CaO)–Na_2O+K_2O–$CaO+FeO+MgO$ of Fig. 11, along with the composition of the rhyolites. The diagram shows that a variety of rocks could give crustal melts, similar to the rhyolites. In particular, rocks of amphibolitic and basaltic to andesitic composition, melted under pressure of 0.1–2.2 GPa and temperature of 900–1050 °C (Beard & Lofgren 1991; Rapp et al. 1991; Rapp & Watson 1995), gneisses, melted under pressure of 0.1–1.5 GPa and temperature of 825–1040 °C (Beard et al. 1994; Gardien et al. 1995), as well as pelites and greywackes, melted under pressure of 0.1–0.7 GPa and temperature of 825–950 °C (Vielzeuf & Holloway 1988; Gardien et al. 1995; Patino Douce & Beard 1996; Montel & Vielzeuf 1997), can produce such melts.

Conclusions

The Evros volcanic rocks, comprising acid and intermediate types, have chemical characteristics typical of orogenic domains and belong to the calc-alkaline and high-K calc-alkaline rock series with some samples exhibiting shoshonite composition. They are closely associated with the formation of fault-controlled sedimentary basins, formed in an extensional regime.

Their chemical composition ranges from basaltic andesite to rhyolite through andesite, trachyandesite, trachydacite and dacite. The basaltic andesites have ortho- and clinopyroxene, while the andesites are pyroxene and hornblende-biotite rocks. The dacites have mostly biotite and hornblende. The rhyolites have mainly biotite and rarely hornblende.

On basis of K/Ar geochronology two main periods of volcanic activity, an Oligocene (33.4–25.4 Ma) and a Early Miocene (22.0–19.5 Ma), could be broadly distinguished. The volcanism should have started earlier, probably in the Middle to Late Eocene, since volcanic products are intercalated with Priabonian clastic sediments.

Two main groups of rocks have been distinguished, the PxBt group with pyroxenes and biotite as the main ferromagnesian mineral constituents, and the HblBt group having hornblende and biotite. The two groups establish their own geochemical trends, which are cross-cutting, parallel or subparallel, indicating different evolutionary histories for them.

The Sr isotopic composition ranges between 0.7057 and 0.7074 in the PxBt group, and between 0.7071 and 0.7080 in the HblBt group.

The PxBt group could be the result of an MFC process in which basaltic andesite and trachydacite represent the basic and the acid end-members respectively. MFC between a basic end-member with a composition similar to that of the HblBt andesites, and an acid end-member with rhyolitic composition, could be the possible processes for the evolution of the HblBt group although AFC is not excluded. The parental magmas for the evolution of the PxBt group are the products of partial melting of an inhomogeneous and strongly metasomatized mantle after having been slightly modified.

The parental magma of the HblBt group could be a hybrid magma of the PxBt group, which evolves, under different conditions to give the HblBt group rocks. Although the involvement of a mantle component cannot be excluded for the origin of the rhyolitic melts, it is suggested that partial melting of crustal material (amphibolite, basalt, andesite, gneisses, pelites, greywackes) under various P-T conditions could give melts similar to the composition of the less evolved rhyolites.

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