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Geochemical and Sr–Nd isotopic evidence for the genesis of the Late Cainozoic Almopia volcanic rocks (Central Macedonia, Greece)

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Summary

Major and trace element contents and Sr–Nd isotope ratios of selected volcanics of Pliocene age from the Almopia area, central Macedonia, Greece, have been determined. These rocks are mainly distinguished as two groups based on geographical, petrological and isotopic data: a) the east–central western group (E–CW) and b) the south western group (SW). The absence of contemporaneous basic volcanics in the Almopia area coupled with the considerable scatter of elements in variation diagrams rule out fractional crystallization as the dominant differentiation process. Instead, disequilibrium textures along with the positive correlation of Sr-isotope ratios with differentiation suggest mixing between a basic and an acid component combined with assimilation and fractionation.

The spider diagrams of the most silica-poor volcanics show evidence of subduction-related processes, indicating that the parental magmas may have been derived from partial melting of mantle wedge enriched in LILE and LREE by subducted slab-derived fluids. Previous data on the oxygen isotope composition of the same volcanics are consistent with this genetic hypothesis. Lastly, the relatively high $^{87}Sr/^{86}Sr$ and low $^{143}Nd/^{144}Nd$ ratios (0.7080 and 0.512370, respectively) of the volcanic sample inferred to be compositionally the closest one to the parental magma of Almopia rocks suggest that the incompatible element enrichment of the mantle source is old, probably of Proterozoic age.

Introduction

The Almopia volcanic rocks (AVRs) are located in the Voras Mountains, central Macedonia, Greece (Fig. 1). They belong to the widespread volcanic activity, which affected the Aegean and the surrounding areas since the Tertiary (*Fytikas* et al., 1984). This volcanism is generally related to the subduction of the African plate underneath the southern margins of the Eurasian plate (*Boccaletti* et al., 1974).

Unlike for volcanics from the southern and central Aegean, there are few isotopic studies on Tertiary and Quaternary volcanics from the northern Aegean (e.g. *Kolios* et al., 1980; *Fytikas* et al., 1984; *Eleftheriadis*, 1989, 1991), though this area is critical for understanding the geodynamic significance of recent magmatism on the southern margin of Europe. In view of this, the study of the AVRs is particularly interesting because the Almopia area lies north of the main fault line system extending from the Aegean through northern Anatolia to the Caspian Sea. The AVRs have an intermediate chemical character and are enriched in potassium and other LILE (*Soldatos*, 1955; *Mercier*, 1968; *Clapsopoulos*, 1991). Petrological and mineralogical data illustrate the high-K calc-alkaline to shoshonite nature of these rocks (*Kolios* et al., 1980; *Eleftheriadis*, 1988). Consideration of all these aspects has prompted the study reported in this paper of representative lithotypes of Almopia volcanism, coupling elemental geochemistry and Sr and Nd isotopes.

Geological setting

The AVRs were emplaced over the Alpine metamorphic basement of the Almopia series, which geotectonically belongs to the Axios (Vardar) zone (*Mercier*, 1968),

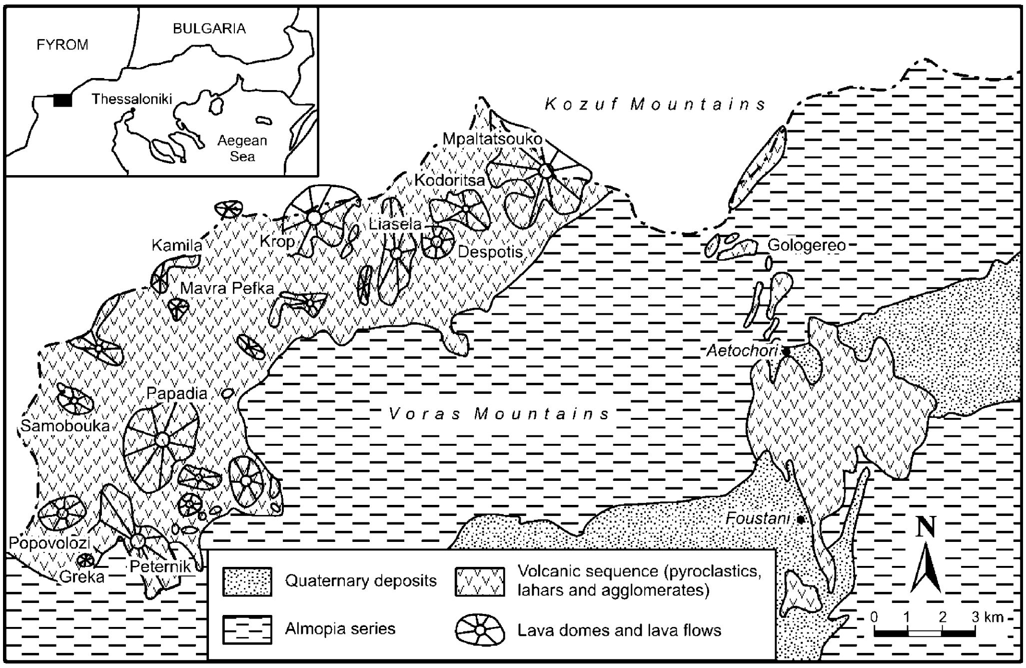

Fig. 1. Simplified geological map of the Almopia volcanic area, central Macedonia (modified after *Kolios* et al., 1980)

consisting mainly of greenschists, phyllites, limestones, gneisses, amphibolites, marbles and ophiolitic rocks.

The AVRs are associated with transversal NE–SW and NNW–SSE faults (*Pavlides* et al., 1990). An extensional tectonic regime has been active in this area since the Neogene. The AVRs form several distinct centers (Fig. 1), which extend northward to the FYROM territory, and consist of lava domes and subordinate lava flows and dikes. A characteristic feature of Almopia volcanism is the intense explosive activity and the domination of volcanoclastic materials (see *Vougioukalakis*, 1994).

Dark-colored, microgranular enclaves occur in almost all AVRs. These enclaves range from a few centimeters to half a meter in diameter in the east–central western area, while they are usually less than ten centimeters in the south-western area.

Based on pollen spores found in tuffs *Mercier* and *Sauvage* (1965) suggested an Upper Pliocene age for Almopia volcanism. This suggestion is supported by the K/Ar dating on whole rocks and on biotite and hornblende separates, indicating emplacement ages from 1.8 to 5.0 Ma (*Bellon* et al., 1979; *Kolios* et al., 1980).

Sampling and petrography

The studied samples were collected from the main volcanic centers and cover the whole spectrum of petrological types. They can be clustered into two groups: the east–central western (E–CW) group represented by samples GOL-7, ML-3, DES-5, LIAS-3 and KAM-21 from the volcanic centers of Gologereo, Kodoritsa, Despotis, Liasela and Kamila, respectively, and the south western (SW) group composed of samples SA-5, PAP-2, PET-3 and PV-1 from the volcanic centers of Saligari (north of Papadia), Papadia, Peternik and Popovolozi, respectively (Fig. 1). Lastly, enclave MPA-18E was selected from the E–CW area.

The AVRs have distinct porphyritic texture and are characterized mainly by the presence of mostly tabular sanidine megaphenocrysts, up to 10 cm in length. They are classified on the basis of their alkali-silica (TAS) relationships (*Le Maitre*, 1989) as trachyandesites (latites) (SA-5, ML-3, GOL-7) and trachytes (PET-3, PV-1, PAP-2, DES-5, LIAS-3, KAM-21), while the enclave (MPA-18E) falls in the field of basaltic trachyandesite. The trachytes fall into two types based on geographical, mineralogical, textural and chemical criteria. Type A trachytes belong to the SW group and are represented by samples PET-3 and PV-1 of K/Ar radiometric ages close to 2 Ma. They are rich in K_2O and include clinopyroxene and biotite phenocrysts set in a holocrystalline groundmass with fluidal texture. Rare olivine crystals occur in some samples. Both plagioclase and sanidine phenocrysts are mantled by K-feldspar of similar composition to the sanidine laths. Type B trachytes from the E–CW group are represented by samples DES-5, LIAS-3 and KAM-21 and have K/Ar radiometric ages, from about 4 to 5 Ma. In contrast to type A trachytes, they consist of hornblende, biotite and subordinate clinopyroxene set in a nearly holocrystalline isotropic groundmass. On chemical grounds sample PAP-2 (trachyte) belongs to the SW group but texturally resembles type B trachytes; its ferro-magnesian minerals comprise only biotite. Trachyandesite SA-5 resembles the type A trachytes both texturally and mineralogically, whereas trachyandesites ML-3 and GOL-7 resemble type B trachytes. Common accessories in all rocks are apatite, titanite, zircon and magnetite.

Enclaves display porphyritic texture and have similar mineralogy with their host rocks, yet they contain a significantly higher proportion of ferro-magnesian minerals. In some samples both biotite and phlogopite occur.

Plagioclase phenocrysts (An_{25}–An_{55}) occur in all rocks and are strongly zoned showing normal and oscillatory reverse zoning. Patchy zoning and sieve-like textures are not rare. Sanidine is compositionally Or_{50-70}. Colorless to dark-green clinopyroxene phenocrysts usually show optically and chemically normal and reverse zoning. Sometimes, crystals with different zoning patterns occur in the same thin section (*Eleftheriadis*, 1988). Biotite is ubiquitous, showing intensive pleochroism in the shade of straw yellow to dark brown-reddish. Hornblende of brownish-green to yellow-brown color (oxyhornblende) constitutes the major ferro-magnesian phase in the E–CW rocks. Like biotite, hornblende is often marginally or completely opacitized. Lastly, a few resorbed quartz phenocrysts occur in sample GOL-7.

Analytical methods

Major and trace element contents were determined at the universities of Cologne and Manchester by XRF techniques (*Brown* et al., 1973). Loss on ignition (LOI) was determined by calcining the sample for 2 hours at 1050 °C in an electric furnace. Representative samples with low silica content have been analyzed by ICP-MS for REE and selected trace elements at the laboratories of CNRS, Nancy, France. The Sr- and Nd-isotope analyses were carried out at Centro di Studio per il Quaternario e l' Evoluzione Ambientale, CNR, Roma. Samples were first dissolved in a mixture of ultrapure HF and HNO_3 in teflon vessels at 70 °C for 48 h. The solutions were then dried and the residues redissolved in 6.2 N ultrapure HCl for 12 h at 70 °C. Sr was separated on a 3 ml AG 50W-X8 resin column, while the separation of Nd from the REE was performed by reversed ion exchange chromatography, using HDEHP as the stationary phase. Isotopic data were collected by a Finnigan MAT 262RPQ mass spectrometer in static mode using Re-double filament. In-run statistics are given at 2-sigma confidence level; repeated analyses of standards gave the following results: NBS987, $^{87}Sr/^{86}Sr = 0.710225$ (10) ($n = 20$); La Jolla, $^{143}Nd/^{144}Nd = 0.512845$ (10) ($n = 15$). No corrections were applied to the measured ratios for instrumental bias. Lastly, oxygen isotope analyses were carried out at the Case Western Reserve University, Cleveland Ohio, USA (see *Eleftheriadis*, 1995).

Analytical results

Table 1 lists major and trace element contents in the rocks studied, while Table 2 presents the Sr- and Nd-isotope ratios as well as $\delta^{18}O$ values determined by *Eleftheriadis* (1991).

The SiO_2 contents in the E–CW volcanics range from 62.7 to 65.7 wt.% except for enclave MPA-18E showing 54.1 wt.%. The SW volcanics have SiO_2 contents ranging from 58.7 to 61.3 wt.%, except for sample SA-5 which has 54.0 wt.%.

Table 1. *Whole-rock geochemical data for the Almopia samples analysed for Sr–Nd isotopes (XRF: Major and trace elements, ICP-MS: REE, Mo, Sb, As)*

Sample	East–Central western group (E–CW)						South western group (SW)			
	MPA-18E Enclave	GOL-7 Trachyand.	ML-3 Trachyand.	DES-5 Trachyte	LIAS-3 Trachyte	KAM-11 Trachyte	SA-5 Trachyand.	PET-3 Trachyte	PV-1 Trachyte	PAP-2 Trachyte
SiO_2 (wt.%)	54.08	62.69	63.03	64.80	64.94	65.71	53.96	58.73	60.00	61.31
TiO_2	1.14	0.45	0.65	0.43	0.45	0.46	0.73	0.64	0.61	0.58
Al_2O_3	19.80	16.90	16.33	16.30	16.79	16.54	17.16	17.23	17.66	17.44
Fe_2O_{3t}	7.34	3.52	4.76	3.34	2.86	2.95	5.65	4.42	3.91	4.00
MnO	0.14	0.08	0.11	0.08	0.01	0.07	0.14	0.13	0.11	0.06
MgO	3.86	2.22	2.13	1.36	1.15	0.90	3.73	2.41	2.07	1.22
CaO	5.48	4.86	4.83	4.01	3.45	2.36	7.37	4.46	3.60	2.66
Na_2O	2.38	4.32	3.63	4.60	4.65	4.22	3.91	3.90	4.42	4.33
K_2O	3.42	3.61	3.82	4.05	4.95	5.27	5.80	6.42	6.58	5.87
P_2O_5	0.63	0.21	0.35	0.24	0.24	0.26	0.62	0.47	0.33	0.43
LOI	2.23	0.88	1.00	0.64	0.45	1.33	1.45	0.90	0.71	1.50
Total	100.51	99.74	100.64	99.86	99.94	100.07	100.52	99.71	100.00	99.41
Rb (ppm)	114	121	126	192	210	229	184	283	270	260
Cs	9						15	29		9
Be	5						7	11		7
Sr	1514	1234	1283	905	914	761	2383	1174	1119	1101
Ba	2237	1510	1550	945	1236	823	2365	1467	1329	1713
Ga	24						21	23		22
Y	25	18	19	22	22	23	27	30	33	39
Ge	1.4						1.3	1.5		1.3
Zr	114	271	282	256	254	355	515	496	382	332
Hf	4						8	10		9
U	6						20	19		28
Th	29						68	64		78
Sn	2						3	4		5
Nb	5	7	8	9	10	15	20	18	17	14
Ta	0.8						1.6	1.5		2.1
Ni	13	17	16	9	7	10	29	11	18	12
Co	23						47	23		16

(*continued*)

Table 1 (*continued*)

Sample	East–Central western group (E–CW)						South western group (SW)			
	MPA-18E Enclave	GOL-7 Trachyand.	ML-3 Trachyand.	DES-5 Trachyte	LIAS-3 Trachyte	KAM-11 Trachyte	SA-5 Trachyand.	PET-3 Trachyte	PV-1 Trachyte	PAP-2 Trachyte
Cr	19	34	46	30	28	32	49	34	33	36
Pb	42						96	81		94
Bi							0.6	0.2		1.3
Zn	95	59	73	61	59	56	84	65	60	63
Cu	30	25	25	12	13	9	44	43	30	45
V	191	42	61	45	36	35	101	67		
Sc		9	9	10	6	4	17	6		
Mo	0.4						1.6	1.7		1.1
As	2.3						19	3.7		13
Sb	0.4						1.2	0.4		1
La*	(131)	(15)	(54)	(41)	(42)	(61)	125 (108)	109 (96)	(82)	84 (71)
Ce*	(220)	(70)	(107)	(74)	(102)	(118)	240 (216)	199 (207)	(179)	155 (144)
Pr	27						27	23		17
Nd*	(99)	(35)	(61)	(47)	(47)	(60)	100 (125)	78 (95)		60
Sm	14						14	12		9
Eu	3						3.2	2.6		2.1
Gd	8						8	8		6
Tb	1.1						1	1		0.8
Dy	5.5						5.3	5.1		4.2
Ho	0.9						0.8	0.8		0.7
Er	2.5						2.3	2.3		2
Tm	0.34						0.31	0.33		0.28
Yb	2.3						2.1	2.2		1.9
Lu	0.35						0.33	0.36		0.31

PET Peternik; *PV* Popovolozi; *PAP* Papadia; *DES* Despotis; *LIAS* Liasela; *KAM* Kamila; *SA* Krop; *ML* Kodoritsa; *GOL* Gologereo; *MPA* Mpaltatsouko (location names refer to Fig. 1)

*For La, Ce and Nd the number in parentheses represent ppm values obtained by XRF

Table 2. *Whole-rock Rb–Sr, Sm–Nd and* $\delta^{18}O$ *(SMOW ‰) isotopic data of the Almopia volcanic rocks*

Sample		SiO_2 (wt.%)	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr \pm 2se$	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd \pm 2se$	$\delta^{18}O$ (‰)
East–Central western group (E–CW)											
MPA-18E	Enclave	54.08	114	1514	0.075	0.708160 ± 08	14	99	0.085	0.512337 ± 05	
GOL-7	Trachyandesite	62.69	121	1234	0.295	0.708782 ± 09		35		0.512340 ± 03	8.6
ML-3	Trachyandesite	63.03	126	1283	0.098	0.708876 ± 08		61		0.512315 ± 03	8.1
DES-5	Trachyte	64.80	192	905	0.614	0.709159 ± 05		47		0.512320 ± 03	7.7
LIAS-3	Trachyte	64.94	210	914	0.665	0.709039 ± 06		47		0.512314 ± 04	
KAM-11	Trachyte	65.71	303	761	1.152	0.709141 ± 06		60		0.512293 ± 11	7.8
South western group (SW)											
SA-5	Trachyandesite	53.96	184	2383	0.223	0.708000 ± 05	14	100	0.084	0.512370 ± 03	7.3
PET-3	Trachyte	58.73	283	1174	0.698	0.709720 ± 13	12	78	0.093	0.512252 ± 05	7.2
PV-1	Trachyte	60.00	270	1119	0.698	0.709897 ± 05				0.512260 ± 08	7.5
PAP-2	Trachyte	61.31	260	1101	0.683	0.708793 ± 06	9	60	0.090	0.512334 ± 05	7.4

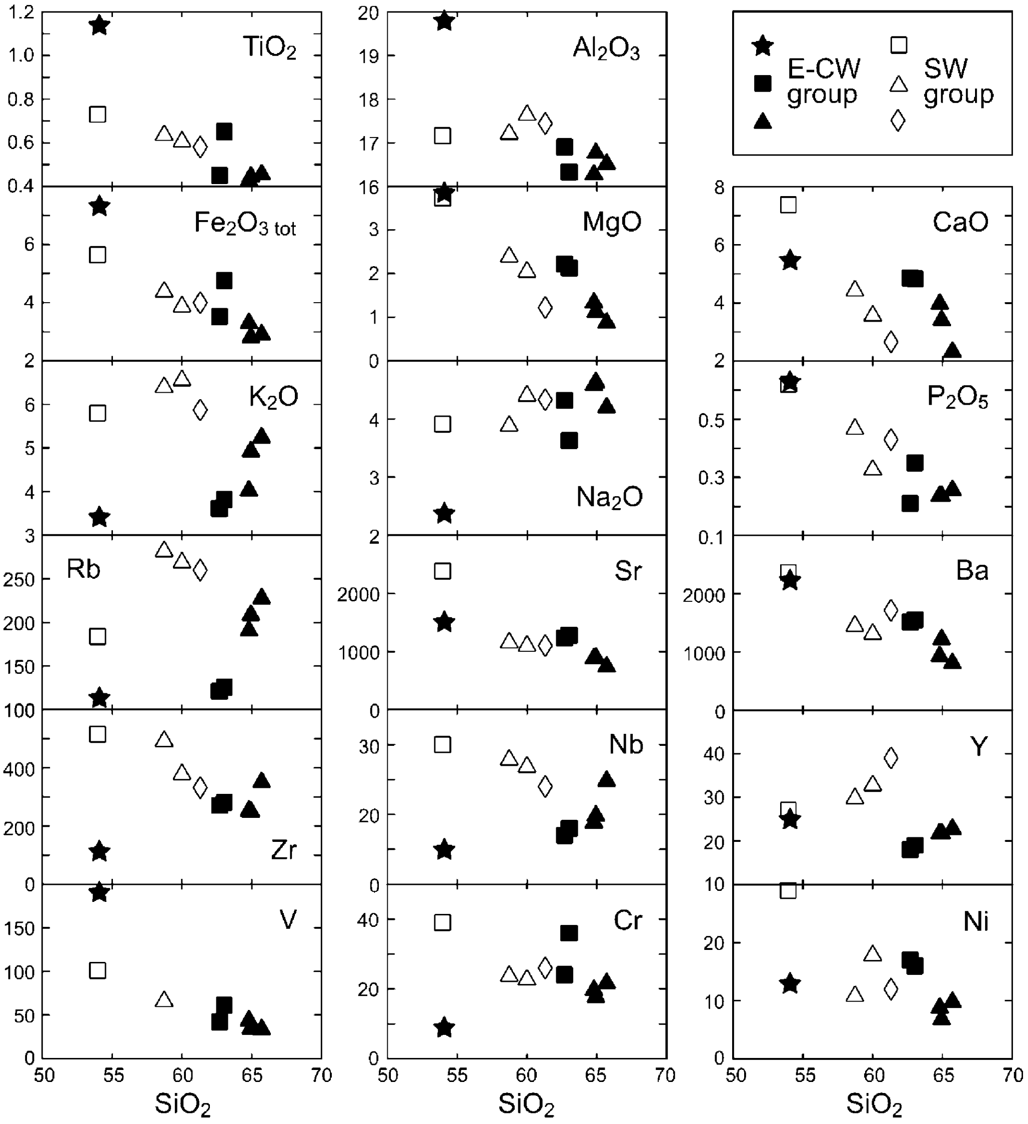

Fig. 2. Major (wt.%) and selected trace element (ppm) vs. silica diagrams for the Almopia volcanic rocks

Beside silica, sample SA-5 and enclave MPA-18E show also similar MgO, MnO and P_2O_5. In contrast, sample SA-5 has comparatively more CaO, K_2O and Na_2O, and less Al_2O_3, Fe_2O_{3tot} and TiO_2.

The diagrams of major oxides and selected trace elements versus silica for all studied rocks are depicted in Fig. 2. It is apparent that, disregarding enclave MPA-18E, all rocks generally exhibit negative correlations between silica and TiO_2, Fe_2O_{3tot}, MgO, CaO, P_2O_5, Sr, Ba, V, Ni, and Zr, respectively, while they have a positive correlation between silica and Na_2O and Rb, respectively, and, lastly, Al_2O_3 remains nearly unchanged. Considering the trachytes, it appears that Fe_2O_{3tot}, TiO_2, P_2O_5, Sr, Ba, Ni and V follow roughly uniform trend, while MgO, CaO, K_2O, Rb, Y and Nb form two trends separating type B trachytes from

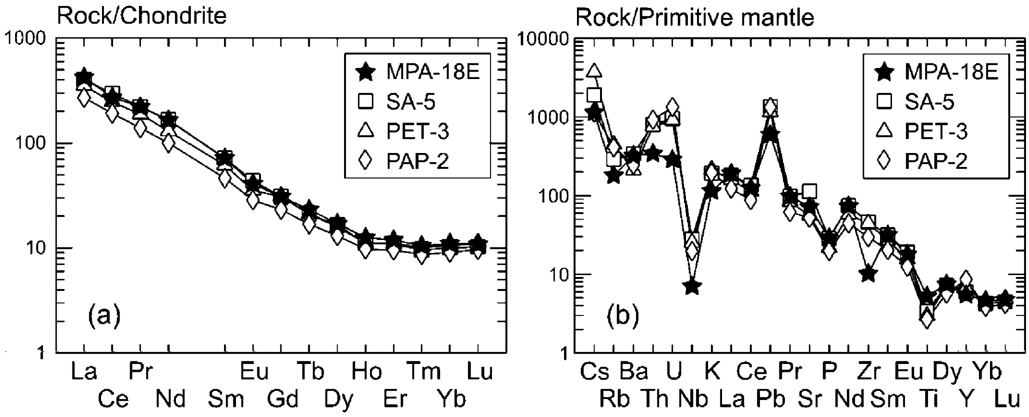

Fig. 3. **a** Chondrite normalized REE patterns for the Almopia volcanic rocks. Chondrite values after *Boynton* (1984). **b** Primitive mantle normalized trace element diagram for the Almopia volcanic rocks. Normalization factors after *Sun* and *McDonough* (1989)

type A trachytes. Sample PAP-2 is compositionally closer to type A trachytes than to type B trachytes.

In Fig. 3a all four rocks display similar REE patterns normalized to chondrite (*Boynton*, 1984) characterized by significant LREE and MREE enrichment (200–400 × chondrite), relatively low abundance in HREE and small negative Eu anomalies (0.77–0.85). Moreover, the REE abundance decreases with increasing silica from sample SA-5 and enclave MPA-18E of close values through sample PET-3 to sample PAP-2.

Figure 3b shows the spider diagrams of the same four rocks analyzed for REE, and normalized to primitive mantle (*Sun* and *McDonough*, 1989). It is apparent that all rocks exhibit negative-slope patterns with significant negative Nb, P and Ti anomalies, and a pronounced positive Pb anomaly.

The measured Sr-isotope ratios range from 0.708000 (sample SA-5) to 0.709897 (sample PV-1), while the measured Nd-isotope ratios range from 0.512252 (sample PET-3) to 0.512370 (sample SA-5) (Table 2). The corresponding isotope ratios for enclave MPA-18E are 0.708160 and 0.512337, respectively. Therefore, sample

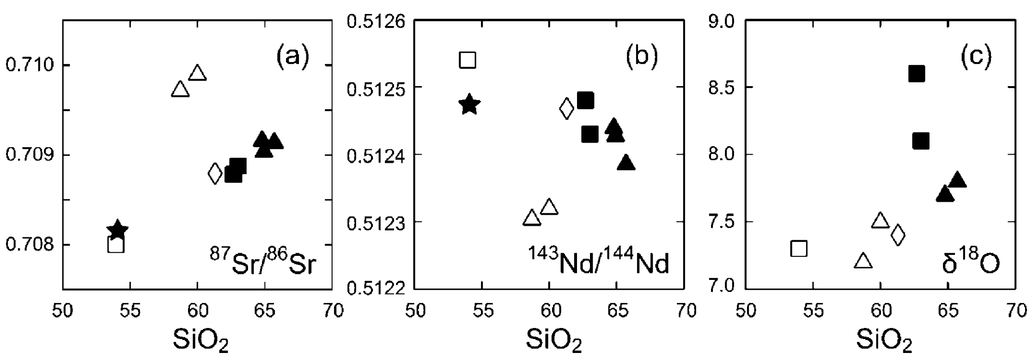

Fig. 4. **a** Sr-isotope ratios, **b** Nd-isotope ratios and **c** $\delta^{18}O$ vs. silica diagrams for the Almopia volcanic rocks. Symbols as in Fig. 2

SA-5 shows the lowest Sr- and the highest Nd-isotope ratio coupled with the lowest SiO_2 content. The measured Sr- and Nd-isotope ratios have not been corrected for the K/Ar radiometric ages (*Bellon* et al., 1979; *Kolios* et al., 1980); as the corrections overlap the corresponding analytical errors, the measured ratios are also taken as the initial Sr- and Nd-isotope ratios.

The $\delta^{18}O$ range from 7.2 (sample PET-3) to 8.6 (sample GOL-7) ‰ (*Eleftheriadis*, 1991) (Table 2).

Lastly, Fig. 4 shows the plots of Sr, Nd and O isotope ratios versus SiO_2. As it is shown from this figure the Sr and O isotopes exhibit overall positive correlations with silica, while the Nd isotopes show negative correlation.

Discussion

The negative correlations between SiO_2 and TiO_2, Fe_2O_{3tot}, MgO, CaO, P_2O_5, Sr, Ba, V, Ni and Zr, respectively (Fig. 2), may be taken as evidence, that the AVRs evolved by fractional crystallization (FC) involving mafic minerals, Ca-rich plagioclase and accessory minerals. The positive correlations between SiO_2 and Na_2O and Rb, respectively, support this hypothesis, as these oxides and Rb generally behave incompatibly.

There are, however, two constraints against FC as the dominant process of differentiation such as: i) the absence of contemporaneous basic rocks in the study area, and ii) the significant scatter of elements in the variation diagrams (Fig. 2). Furtheremore, the two trends observed for MgO, CaO, K_2O, Rb, Y and Nb versus SiO_2 indicate that the volcanic rocks of E–CW group are not linked with those of the CW group through FC. This conclusion is in agreement with the fact that the rocks of the former more felsic group are significantly older than those of the latter group (see *Kolios* et al., 1980). Nevertheless, field and structural considerations indicate that all AVRs could have shared similar parental magmas because of the relatively similar mineral composition and the presence of basic enclaves.

The Sr-, Nd- and O-isotope versus silica variations depicted in Fig. 4 are further evidence against differentiation purely via FC. Instead, these correlations suggest differentiation through fractional crystallization plus assimilation (AFC) (*De Paolo*, 1981) of crustal materials rich in SiO_2, radiogenic Sr, non-radiogenic Nd and ^{18}O. It is well known that AFC may affect especially magmas emplaced through a relatively thick crust (Macedonia crustal thickness >30 km). Moreover, the existence of a negative correlation between Sr- and Nd-isotope ratios (Fig. 5) supports the hypothesis of magmatic evolution of both groups via AFC. In view of this, Fig. 5 shows the best-fit AFC trajectory between an end member represented by sample SA-5 as representative of the AVRs parental magma, and another member, represented by average Alpine crustal basement (*von Blanckenburg* et al., 1992). The model shows that magmatic differentiation of the AVRs may result by a relatively low ($r = 0.3$, *De Paolo*, 1981) assimilation-fractionation ratio. Taking into account the differences between the two groups (age, mineralogy, geochemistry etc.) we might consider the AFC curves (Fig. 5) not as a continuous evolution process for the whole AVR series; they rather indicate that the two groups can be derived by the same initial magma through different degrees of crystallization. Alternatively, the widespread microgranular enclaves, representing

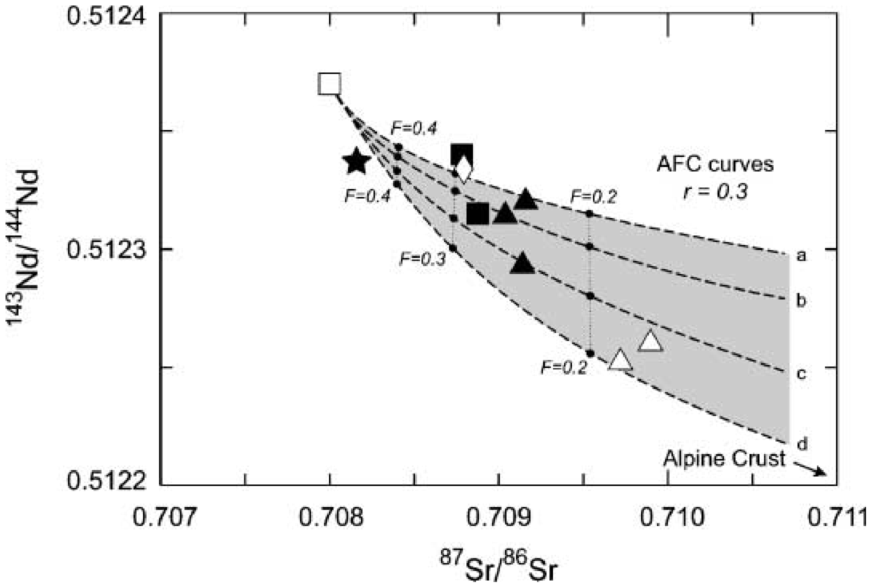

Fig. 5. $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$ compositions of the Almopia volcanic rocks. AFC calculations (*De Paolo*, 1981) have been performed using the following parameters: uncontaminated magma (sample SA-5): Sr = 2383 ppm, Nd = 100 ppm, $^{87}Sr/^{86}Sr = 0.708$, $^{143}Nd/^{144}Nd = 0.51237$; contaminant (Alpine crust): Sr = 100 ppm, Nd = 20 ppm, $^{87}Sr/^{86}Sr = 0.718$, $^{143}Nd/^{144}Nd = 0.51210$, $r = 0.3$, $D^{Sr} = 2$, $D^{Nd} = 1.2$ (curve a), 1.4 (curve b), 1.7 (curve c) and 1.9 (curve c). Symbols as in Fig. 2

blobs of basic magma, the disequilibrium phenomena of plagioclase (patchy zoning, sieve-like textures), the existence in the same thin section of clinopyroxene phenocrysts with both normal and reverse zoning, and particularly the occurrence of resorbed quartz phenocrysts may suggest binary mixing between a basic melt such as the parental magma of sample SA-5 and an acid melt, which might be derived by partial melting of average Alpine crustal basement (*von Blanckenburg* et al., 1992). The spread of the elemental and isotopic data coupled with the observed trends suggest that magmatic differentiation of the AVRs involved mixing between a basic and an acid component combined with assimilation and fractional crystallization.

The Neogene extensional tectonic regime responsible for the NE–SW faults (*Pavlides* et al., 1990) facilitated melting and empacement of Almopia lavas. Heating of the lithospheric mantle following thinning probably caused the partial melting of the metasomatized mantle (cf. *Turner* et al., 1996).

Geodynamic setting

As the chemical and isotopic characteristics of the AVRs indicate that sample SA-5 is likely to be the closest to the original parental magma of these rocks, we have tried to constrain the characteristics of the magma source on the basis of both the chemical and isotopic composition of this sample. In view of this, it is noted that sample SA-5 shows MgO, Fe_2O_{3tot} and CaO contents of melts generated in the upper mantle, but, in contrast, it shows relatively low Co, Ni and Cr. These features may mean that the parental magma underwent fractionation of spinels with negligible crustal contamination before eruption. The small negative Eu anomaly of this sample (Fig. 3a) probably refers to variation of oxygen fugacity in the magma more than to plagioclase fractionation during the magma ascent to surface because of the relatively high CaO content in the sample.

Despite evidence of a possible derivation of the parental magma of sample SA-5 from the upper mantle, its spider diagram (Fig. 3b) shows enrichment in K_2O and other LILE, generally uncommon in mantle-derived melts. Nevertheless, such enrichment as well as the high Sr content of this rock (Table 1) cannot be explained by crustal contamination of the parental magma, as contamination was negligible as stated above. Likewise, the Pb, U and Th contents in sample SA-5, being higher than those in average granite (Pb = 30 ppm, U or Th = about 10 ppm, *Wedepohl*, 1974), rule out significant crustal assimilation. Therefore, it is evident that the mantle source of the parental magma of sample SA-5 was anomalously enriched in K_2O and associated LILE (including Sr) with respect to the source of MORB melts. Moreover, because of its strong Nb-depletion the spider diagram of sample SA-5 suggests that there is some link between Almopia magmatism and subduction, as already noted by *Kolios* et al. (1980). In this view, it is uncertain if the enrichment in K and associated elements is related to subduction or not. The origin of negative Nb, Zr and Ti anomalies compared with adjacent elements is commonly attributed to the selective metasomatic modification of the sub-arc highly-depleted mantle by LILE and LREE originating from the subducted slab (*Tatsumi* et al., 1986; *McCulloch* and *Gamble*, 1991; *Hawkesworth* et al., 1991). In contrast, slab melt hybridization should add HFSE to the mantle because small percent partial melting of the slab should mobilize the most incompatible elements (e.g. *Kesson* and *Ringwood*, 1989). As a whole, considering the relatively high LILE/HFSE ratio of sample SA-5, it is suggested that the mantle source of the parental magma was metasomatized by slab-derived fluids. In this view, the enrichment in K and associated elements characteristic of sample SA-5 is explained by a very low degree of partial melting of metasomatized mantle source, containing phlogopite and/or amphibole (cf. *Foley* et al., 2002).

The affinity of sample SA-5 to subduction-related volcanism finds no support in the geology, as Macedonia was not an active convergent margin during the Late Tertiary. Subduction may have occurred in the Early Tertiary during the closure of the Axios (Vardar) ocean because of the collision of Africa and Eurasia. In this view, the time span elapsed (more than 40 Ma) between the closure of the Axios ocean and the start of Almopia volcanism is probably too large, compared with that commonly accepted for subduction-related magmatism.

The relatively high Sr- and low Nd-isotope ratios measured in sample SA-5 (Fig. 6) can be used to place new constrains on the nature of the source of Almopia volcanism. In fact, the isotopic ratios, which cannot result from negligible continental crustal assimilation by the parental magma of this sample, are, however, not typical of magmas related to common subduction. The Sr- and Nd-isotope ratios of sample SA-5 (and the other AVRs) lie between DM and EMII mantle component (*Zindler* and *Hart*, 1986). This could suggest that the parental magma of sample SA-5 was derived by mixing between melts of depleted mantle and those from an enriched mantle source. Therefore, if the characteristic signature of sample

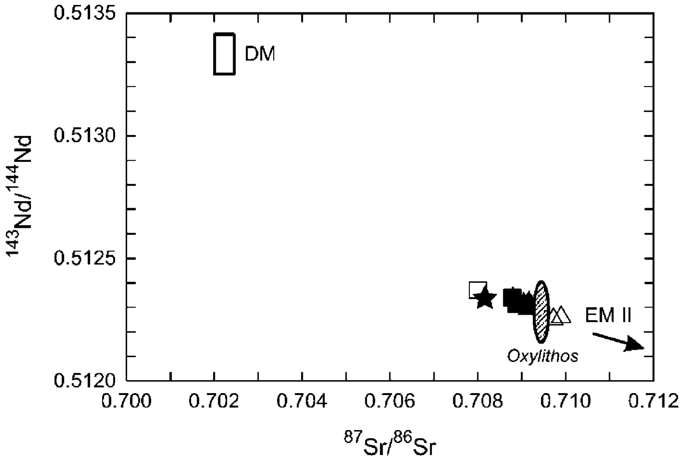

Fig. 6. Sr and Nd isotope variation for the Almopia volcanic rocks. DM, depleted mantle; EM II, enriched mantle (*Zindler* and *Hart*, 1986). Symbols as in Fig. 2. Shaded area, volcanic rocks from Oxylithos, Euboea (*Barbieri* et al., 1998)

SA-5 is inherited from depleted mantle metasomatically modified by slab-derived fluids, the responsible subduction was probably much older than Early Tertiary. A significantly old metasomatic mantle source may, in fact, be characterized by relatively high levels of radiogenic Sr- and, conversely, low Nd-isotope ratios. It should be noted that similar volcanic rocks from the Tibetan plateau (*Turner* et al., 1996) and East Antarctica (*Andronikov* et al., 1998) with comparable Sr and Nd isotope ratios have been generated from a lithospheric mantle source subjected to Proterozoic enrichment. In this respect, it is interesting that sample SA-5 has a Nd model age (*Arndt* and *Goldstein*, 1987) of about 800 Ma, calculated with respect to a depleted mantle source. *Pe-Piper* et al. (1998) have suggested a Proterozoic mantle enrichment to account for the geochemical characteristics of Tertiary igneous rocks of northern Greece and similarly, the presence of a long-lived component in the mantle source of the AVR is also consistent with the suggestions of *Robert* et al. (1992) and *Barbieri* et al. (1998) to explain the characteristics of Late Tertiary volcanics from other Aegean areas, such as the K-rich volcanics from Bodrum and Oxylithos, respectively. In particular, the inferred Sr- and Nd-isotope ratios of the mantle source (Fig. 6) are similar for sample SA-5 and Oxylithos volcanics.

Finally, the whole-rock $\delta^{18}O$ of sample SA-5 is higher than the value of 5.8‰ assumed to be representative of common mantle melts (*Taylor*, 1968). However, the $\delta^{18}O$ falls into the range for subduction-related magmas, including those emplaced in a primitive island arc, i.e., intra-oceanic setting. These latter tend to have higher $\delta^{18}O$ than magmas derived from depleted mantle sources like MORB, as result of subducted altered oceanic crust contributing to the overlying mantle wedge (*Hawkesworth*, 1982). Moreover, the $\delta^{18}O$ of sample SA-5 also falls into the range of primitive K-rich volcanics of Pliocene–Pleistocene age from Italy (5.5–7.5‰, *Ferrara* et al., 1986), the origin of which is inferred from mantle sources enriched in radiogenic Sr. As a whole, though the $\delta^{18}O$ of sample SA-5 cannot identify unambiguously the components present in the magma source, at least it does not contrast with the genetic hypothesis proposed.

Conclusions

Geographical, petrological and isotopic data facilitate subdivision of the Almopia volcanic rocks into two groups: (i) the east–central western group and ii) the south-western group. On the basis of the alkalis-silica relationship the AVRs are classified into three distinct series, represented by trachyandesites and two types of trachytes, plus an enclave rock of basaltic trachyandesitic affinity. Almost all AVRs are characterized by a K-alkaline signature ($K_2O/Na_2O > 1$).

Assuming that all AVRs derive from a broadly common parental magma, this latter would have chemical and isotopic characteristics close to sample SA-5, which is the least-siliceous rock (54.0 wt.% SiO_2) among those studied. This sample exhibits high contents of K_2O (5.8 wt.%), P_2O_5 (0.62 wt.%), Sr (2383 ppm), Ba (2365 ppm), Rb (184 ppm), Zr (515 ppm), REE ($La/Lu_N = 33$) and Pb (96 ppm). The high contents of K and associated elements, especially Sr and Pb, indicate that the parental magma of this rock did not derive by melting of depleted mantle. Neither of these high contents can result by mere crustal contamination of the parental magma, because sample SA-5 shows for instance relatively high contents of CaO and significant MgO (7.4 and 3.7 wt.%, respectively), which are incompatible with major AFC. Therefore, the high contents of K and associated elements are characteristic of the source of the parental magma. Moreover, the spider diagram of this sample versus N-MORB is characterized by a negative slope and pronounced negative anomalies of Nb, P and Ti, typical of subduction-related magmatism.

It thus is possible that the enrichment in LILE and LREE is due to metasomatism of the mantle wedge by fluids released from a subducted slab. With respect to the timing of subduction, as Macedonia was not an active convergent margin in the late Pliocene, it may be envisaged that some link between Almopia magmatism and subduction occurred in the Early Tertiary during the collision of Africa and Eurasia. However, if metasomatism of the mantle wedge occurred at that time, there is no explanation for the relatively high Sr- and low Nd- isotope ratios of sample SA-5 (0.7080 and 0.512370, respectively). These isotopic ratios may reflect a much older subduction event. In view of this, a Proterozoic subduction may account for providing enough radiogenic Sr and Pb because of Rb and U–Th radioactive decay, respectively.

The enrichment in K and associated elements characteristic of sample SA-5 suggests a very low degree of partial melting of the metasomatized mantle source containing phlogopite and/or amphibole.

The whole-rock $\delta^{18}O$ of sample SA-5 (7.3‰) is far from the range of typical mantle melts, but, it falls within the range of both subduction-related melts, and K-rich Italian Plio–Pleistocene volcanics, the origin of which is thought to be connected with mantle enrichment by radiogenic Sr. Therefore, the $\delta^{18}O$ does not contrast with the genetic hypothesis proposed.

Finally, within each series of the AVRs, the chemical and isotopic compositions suggest that magmatic differentiation was connected with mixing between a basic and an acid component derived by crust melting, combined with crystal fractionation and assimilation.

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