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Occurrence of primary almandine-spessartine-rich garnet and zinnwaldite phenocrysts in a Neogene rhyolite on the island of Chios, Aegean Sea, Greece

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ABSTRACT

Primary almandine and spessartine-rich garnet and zinnwaldite phenocrysts occur along with feldspar (plagioclase and sanidine) phenocrysts, in the rhyolite of Profitis Ilias, which is located on the SE coast of the island of Chios, Greece. The distinctive mineralogical composition of this rhyolite is described. Although formed in the back-arc tectonic environment of the Aegean volcanic arc, the Profitis Ilias rhyolite shows significant trace element compositional differences when compared with typical arc or back-arc volcanic rocks of the area. It shows extreme depletion in Sr and Ba and enrichment in Nb and Mn, and has much more affinity with A-type granites and particularly Li-mica granites.

Apparently, both zinnwaldite and spessartine-rich garnet can be generated as primary phases from a granite melt enriched in volatile constituents at low *P–T*. This granite melt could be the residual product of an un-exposed, earlier formed, typical back-arc granite of the area, enriched in volatile constituents from a subcrustal source above the active mantle of the eastern Aegean area.

The extensive and deep faulting in the broad eastern Aegean lithosphere section would have facilitated the rapid ascent of that volatile-enriched granite melt, the parent of the Profitis Ilias rhyolite.

KEYWORDS: almandine-spessartine-rich garnet, zinnwaldite, Neogene, rhyolite, volcanic, Chios, Aegean Sea, Greece.

Introduction

MAGMATIC garnets have often been recorded as accessory minerals in granitic rocks. The occurrence of garnet microphenocrysts in acid volcanic rocks is less common. Stone (1988) reviews the origin of the garnets in granitic rocks. Three mechanisms for the origin of these garnets have been proposed: (1) assimilation of pelitic material; (2) high-pressure phenocrysts or xenocrysts formed at depth and transported to higher levels; and (3) low-pressure precipitates from a peraluminous fluid. The relative proportions of the various garnet end-members reflects the origin and the chemical evolution of some granitic complexes (Stone, 1988; Harrison, 1988; Whitworth, 1992).

Zinnwaldite has been mainly recorded as an accessory mineral in differentiated 'late-stage' granites and pegmatites and in their associated metasomatic rocks. Most of the Li-micas in granites seem to be late hydrothermal products but it has been shown that some Li-micas may be primary, i.e. crystallized from the melt (Henderson *et al.*, 1989).

The island of Chios is located at the NE part of the Aegean Sea (Fig. 1). The geology of Chios has been studied by many researchers (e.g. Angelier and Tsoflias, 1976; Papanikolaou and Sideris, 1983; Netels and Tsoflias, 1989). Chios consists of two main stratigraphic units. The lower unit (autochthonous) in which Silurian to Devonian blocks predominate and the upper unit (allochthonous), a Carboniferous to Cretaceous nappe. Tertiary, low-K calc-alkaline volcanic rocks of andesitic to dacitic composition cut across and overlie both units. These igneous rocks record the final subduction of a Palaeotethyan oceanic region. Throughout the island of Chios, small Neogene volcanic occurrences exist which

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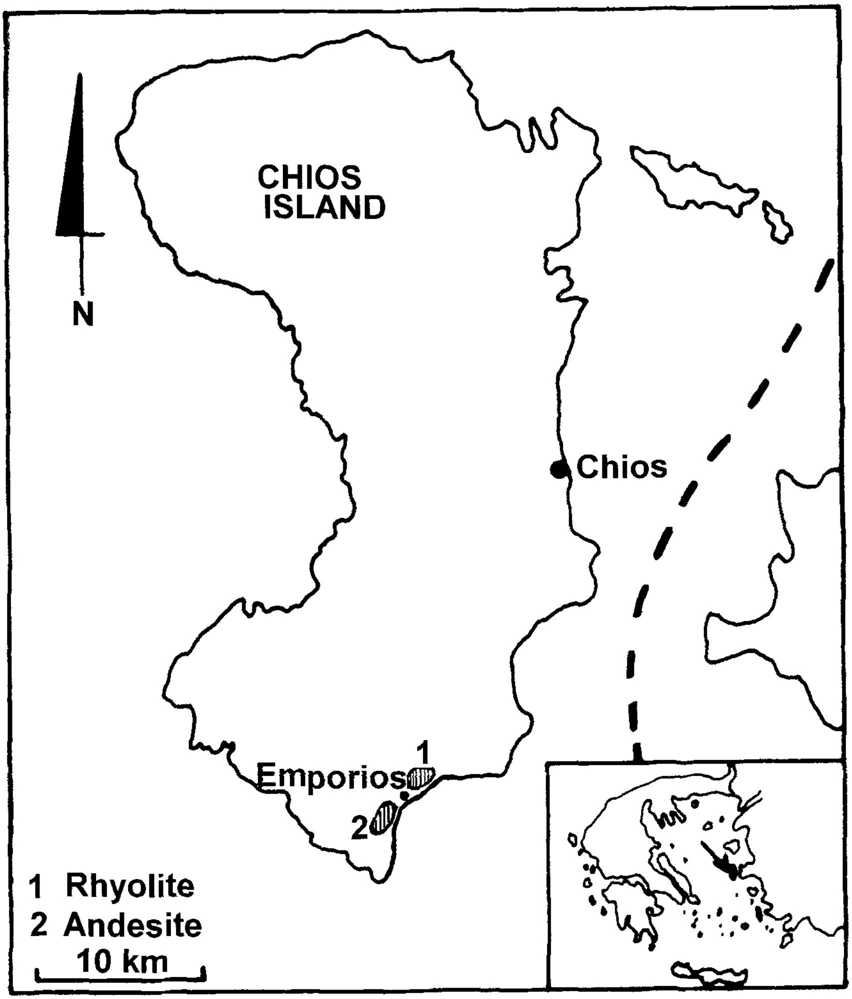

FIG. 1. Sketch map of Chios island, Aegean Sea showing the location of Profitis Ilias rhyolite and the neighbouring andesite.

are either andesitic or rhyolitic in composition (Mitropoulos *et al.*, 1999). In the rhyolite of Profitis Ilias, which is located at the SE part of Chios (Fig. 1), primary garnet and zinnwaldite phenocrysts occur among other (more usual) mineralogical constituents. The unusual mineralogical composition of this rhyolite is the focus of this study.

Sampling and analytical methods

Sampling was from unaltered, well preserved outcrops. The chemical analyses were carried out in the Department of Geology at the University of Leicester, England. The mineral phases were studied using a polarized light microscope and analysed using an automatic electron microprobe (JXA–8600 Superprobe) with the Energy Dispersive method, and with pure elements or natural compounds as standards.

Major and trace element analyses were carried out using an X-ray fluorescence method with a Philips PW 1400 series spectrometer. Details of the analytical procedure, precision and accuracy of the analytical techniques are given in Marsh *et al.* (1983).

Petrography and chemistry

The rhyolite of Profitis Ilias exhibits a porphyritic texture with two generations of phenocrysts in a groundmass consisting of microlitic crystals and glass (Fig. 2). The first phenocryst generation (6 vol.%) consists of euhedral to subhedral sanidine, quartz, garnet, mica and plagioclase crystals, 1–4 mm long and 0.3–0.6 mm wide. The second phenocryst generation (63 vol.%) consists mainly of plagioclase crystals as well as crystals of the first generation minerals, which are 0.1–0.8 mm long and 80–150 μm wide. Both of the phenocryst generations are in a microlitic groundmass consisting of plagioclase and white mica microlitic crystals (23 vol.%) and glass (3 vol.%).

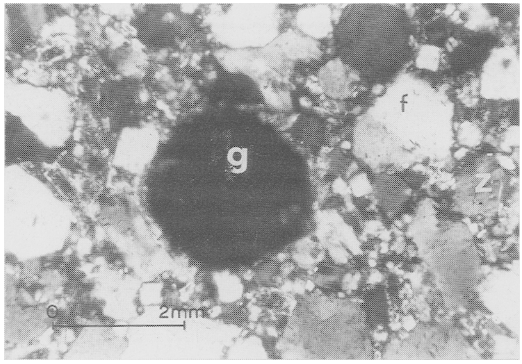

FIG. 2. Photomicrograph (× nicols) of the Profitis Ilias rhyolite.

Representative major and trace element analyses of the Profitis Ilias rhyolite are given in Table 1. The Profitis Ilias rhyolite can be characterized as subalkalic, showing calc-alkaline, but more particularly anorogenic A-type affinity (Eby, 1990). Although it has been generated in a back-arc tectonic environment, the rhyolite shows some unusual compositional characteristics; namely, the mantle normalized diagrams (Fig. 3) are very different from those of the associated andesite, which is of similar age,

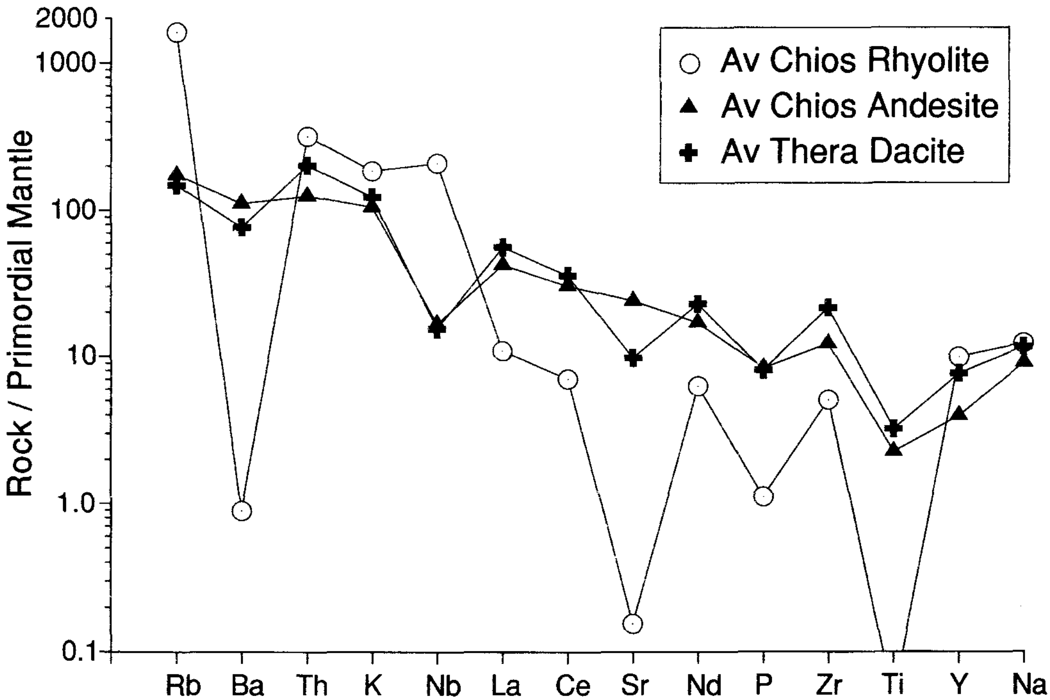

FIG. 3. Multi-element diagram (normalized to primitive mantle: Sun and McDonough, 1989) of the Profitis Ilias rhyolite (open circles), the associated andesite (solid triangles) and that of a typical arc dacite from Santorini (solid crosses).

TABLE 1. XRF analyses of three rhyolites from Chios, with the average composition compared with the associated average andesite (n=4) from Chios and an average dacite (n = 3) from Santorini (Thera) volcano

	Chios rhyolites CH-1	CH-2	CH-3A	average	Chios andesite average	Santorini dacite average
SiO_2	73.90	73.30	73.30	73.50	59.40	62.10
TiO_2	0.01	0.01	0.01	0.01	0.47	0.68
Al_2O_3	14.80	14.8	14.70	14.70	16.10	18.20
Fe_2O_3	0.72	0.75	0.77	0.75	5.02	5.19
MnO	0.11	0.13	0.14	0.13	0.10	0.10
MgO	0.07	0.15	0.11	0.11	4.50	1.50
CaO	0.56	0.62	0.63	0.60	6.60	5.30
Na_2O	4.70	4.60	4.60	4.60	3.40	4.40
K_2O	4.20	4.30	4.30	4.30	2.40	2.80
P_2O_5	0.02	0.02	0.03	0.02	0.17	0.17
LOI	0.53	0.69	0.67	–	–	–
Total	99.62	99.37	99.20			
V	<1	1.5	<1	1.2	99	64
Cr	<1	<1	5	2	149	6
Ni	4	4	9	6	46	8
Zn	113	94	114	107	49	51
Ga	42	41	41	41	18	18
Rb	1117	1099	1089	1102	118	101
Sr	3	4	4	4	568	232
Y	32	45	62	46	19	36
Zr	57	54	58	56	136	238
Nb	157	147	168	158	13	12
Ba	<0.2	<0.2	18	6	760	522
La	7.5	7.9	7.8	8	30	40
Ce	12.4	10.3	16.4	13	56	66
Nd	7.2	9.5	9.2	9	23	31
Th	39	24	29	31	12	19

and is also very distinct from a typical modern dacite from Thera volcano on the island of Santorini. Both the Profitis Ilias rhyolite and the andesite show higher LIL/HFS element ratios than the arc volcanics, as do most volcanic rocks from the back-arc tectonic environment of the Aegean area (Mitropoulos and Katerinopoulos, 1993). In addition, the Profitis Ilias rhyolite is highly depleted in Sr, Ba and Ti, less so in P, but actually shows a strong enrichment in Nb (resulting in marked negative Ba, Sr and Ti anomalies and a positive Nb anomaly). The rhyolite also shows a larger Mn content (0.14%) than the associated andesite (0.09%); these are not characteristics either of the arc and back-arc Aegean volcanics nor of the Cyclades granites formed in the same back-arc tectonic environment (Stouraiti *et al.,* 1998). The rhyolites share many geochemical characteristics with A-type granites (Eby, 1990) such as high Ga, Nb, Zn, Rb and low Ba, Sr, Ti, where it is argued that there is often a mantle component to many such granites. Enrichment in Nb and Mn and deficiency in Sr have been reported in the Cornubian Li-mica granites studied by Stone (1992).

Mineralogy

As has been noted above, the main mineralogical constituents of the Profitis Ilias rhyolite are feldspar (sanidine and plagioclase), quartz, garnet and mica.

Feldspar

Euhedral sanidine crystals appear in both the first and the second phenocryst generations. In some of the sanidine phenocrysts of the second generation there are inclusions of euhedral to subhedral plagioclase crystals, quartz grains and mica flakes. Plagioclase euhedral to subhedral crystals form the main mineral phase of the second phenocryst generation. The composition of the K-feldspars range from $Or_{60}Ab_{40}$ to $Or_{76}Ab_{24}$ while the plagioclase contains up to 85% albite. The composition of the plagioclase inclusions in the sanidine crystals do not differ from that of the plagioclase of the second phenocryst generation. Representative K-feldspar and plagioclase analyses of the Profitis Ilias rhyolite are given in Table 2.

Garnet

The garnet phenocrysts are euhedral to subhedral (Fig. 2). Some of the garnet phenocrysts are rimmed by fine flakes of white mica. Representative analyses of the Profitis Ilias rhyolite garnets are given in Table 3. There is no remarkable compositional zoning from core to margin of these garnets. They are almandine- (50%) and spessartine- (40%) rich with low pyrope content (<1%). The garnets of the Profitis Ilias rhyolite fall within the range of igneous compositions recorded by Miller and Stoddard (1981). Their compositions can be considered as typical of garnets occurring in silicic calc-alkaline volcanic and plutonic rocks (Stone, 1988).

Mica

The euhedral to subhedral mica phenocrysts (Fig. 2) are pale-brown in colour and they do not show any textural signs of having been formed by replacement of an earlier phase. They are thus considered to be primary. Representative analyses of micas are given in Table 4. The Li_2O values were estimated using the regression equations given by Tischendorf *et al.* (1997). The analysed micas plot on the zinnwaldite field on the $FeO-SiO_2$ and $FeO-Al_2O_3-SiO_2$ diagrams (Stone *et al.*, 1988). They also plot in the zinnwaldite field on the (Mg-Li) *vs.* (Fe_{tot}+Mn+Ti-Al^{VI}) diagram for graphical representation of Li-bearing micas introduced by Tischendorf *et al.* (1997). The notable characteristic of the zinnwaldites is their relatively high MnO (up to 4 wt.%).

Discussion

It is important to consider the tectonic environment of the rhyolite in order to define what factors contribute to the unusual almandine-spessartine-rich garnet + zinnwaldite assemblage. The Central Aegean is mainly a calc-alkaline volcanic province, but along the eastern margin of the Aegean and in Western Turkey both calc-alkaline and alkaline volcanic associations occur (Güleç, 1991). Alkaline rocks occur on the Karaburun Peninsula in western Turkey, only 20 km from

TABLE 2. Representative analyses of feldspar from the Profitis Ilias rhyolite

Sample	Ch-104	Ch-106	Ch-107	Ch-109	Ch-82	Ch-85	Ch-100
SiO_2	65.79	65.86	66.46	65.61	65.37	65.09	65.52
Al_2O_3	18.25	20.57	20.12	18.53	18.26	18.26	21.07
CaO	<0.05	1.86	1.49	0.05	0.05	<0.05	2.42
Na_2O	4.25	9.73	9.95	4.5	2.83	2.73	9.74
K_2O	10.82	1.07	1.3	10.52	12.84	13.23	0.71
Total	99.11	99.09	99.32	99.26	99.35	99.31	99.46
Cations of the basis of 8 oxygens							
Si	12.039	11.695	11.778	11.986	12.021	12.001	11.597
Al	3.933	4.302	4.199	3.987	3.954	3.965	4.392
Ca	0.000	0.354	0.283	0.020	0.010	0.000	0.459
Na	1.508	3.35	3.419	1.594	1.009	0.976	3.343
K	2.526	0.242	0.294	2.452	3.012	3.112	0.16
Molar proportions							
Ab	37.4	84.9	85.6	39.2	25.0	23.9	84.4
An	0.0	9.0	7.1	0.5	0.2	0.0	11.6
Or	62.6	6.1	7.4	60.3	74.7	76.1	4.0

TABLE 3. Representative analyses of garnets from the Profitis Ilias rhyolite

Sample	Ch-41	Ch-42	Ch-43
SiO_2	36.25	36.08	36.06
TiO_2	0.05	0.06	0.02
Al_2O_3	19.45	19.38	19.30
Cr_2O_3	0.00	0.04	0.03
FeO^*	21.78	21.93	21.75
$Fe_2O_3{}^*$	2.13	2.13	2.60
MnO	16.72	16.72	17.05
MgO	0.15	0.15	0.12
CaO	3.31	3.06	2.87
Na_2O	0.07	0.06	0.11
Total	99.91	99.61	99.91
Cations on the basis of 12 oxygens			
T_{Si}	2.987	2.985	2.978
T_{Al}	0.013	0.015	0.022
Sum T	3.000	3.000	3.000
Al^{VI}	1.875	1.873	1.855
Fe^{3+}	0.132	0.132	0.161
Ti	0.003	0.004	0.001
Cr	0.000	0.003	0.002
Sum A	2.010	2.012	2.019
Fe^{2+}	1.501	1.517	1.502
Mg	0.018	0.018	0.015
Mn	1.167	1.172	1.193
Ca	0.292	0.271	0.254
Na	0.011	0.01	0.018
Sum B	2.990	2.988	2.981
Total cations	8.000	8.000	8.000
Molar proportions			
Alm	50.39	50.94	50.69
And	6.65	6.68	8.18
Gross	3.16	2.30	0.29
Pyrop	0.62	0.62	0.50
Spess	39.18	39.33	40.24
Uvaro	0.00	0.13	0.10

* Calculated values after Knowles (1987)

TABLE 4. Representative mica (zinnwaldite) analyses from the Profitis Ilias rhyolite

Sample	Ch-101	Ch-102	Ch-112	Ch-92
SiO_2	40.86	42.16	41.94	44.32
TiO_2	0.45	0.34	0.39	0.31
Al_2O_3	22.03	21.6	22.2	20.61
FeO	11.75	12.09	11.59	12.02
MnO	3.93	3.83	4.05	3.56
MgO	0.14	0.27	0.27	0.14
CaO	0.00	0.00	0.00	0.00
Na_2O	0.55	0.47	0.49	0.39
K_2O	9.31	8.45	8.99	8.62
Li_2O^*	2.15	2.52	2.46	3.15
Total	91.17	91.73	92.38	93.12
Cations on the basis of 22 oxygens				
Si	6.18	6.28	6.22	6.46
Al^{IV}	1.82	1.72	1.78	1.54
Al^{VI}	2.10	2.07	2.09	1.99
Ti	0.05	0.04	0.04	0.03
Fe	1.49	1.51	1.44	1.46
Mn	0.50	0.48	0.51	0.43
Mg	0.03	0.06	0.06	0.03
Ca	0.00	0.00	0.00	0.00
Li	1.31	1.51	1.47	1.85
Na	0.16	0.14	0.14	0.11
K	1.80	1.61	1.70	1.60
Z	8.00	8.00	8.00	8.00
Y	5.48	5.67	5.61	5.79
X	1.96	1.75	1.84	1.71

* Calculated values after Tischendorf *et al.* (1997)

Chios Island. According to Seyitoglu *et al.* (1997), extension began in Western Turkey during the Miocene (23 Ma), and alkaline volcanism replaced calc-alkaline volcanism at ~15 Ma. The early alkaline volcanism was mainly potassic (Robert *et al.*, 1992), but changed in western Turkey to become more sodic during the Quaternary (Seyitoglu *et al.*, 1997).

The Chios rhyolites are unlike the calc-alkaline lavas from elsewhere in the Aegean (Fig. 3), but are compositionally similar to A-type granites in showing extreme depletion in Sr, Ba and Ti, and with enhanced Nb, Ga and Zn contents. Similar volcanic rocks to the Chios rhyolites occur on the island of Antiparos in the Cyclades, Central Aegean (McGrath, 1999), and also in the Emet area of western Turkey (Seyitoglu *et al.*, 1997). A-type granites are regarded as the products of crust–mantle interaction (Eby, 1990; Wickham *et al.*, 1996) and this has been the proposed petrogenesis of other magmas in the region (Robert *et al.*, 1992; Seyitoglu *et al.*, 1997; Stouraiti *et al.*, 1998), whether volcanic or plutonic, but such models invoke metasomatic enrichment of the sub-continental lithosphere. In this respect it could be important that the Menderes–Cyclades massif is regarded as a sliver of continental basement (Papanikolaou, 1989), and thus could have been accreted to the Greek continent with its subcontinental lithosphere still intact. This may have been responsible for the more alkaline (potassic) character of the volcanism in the eastern Aegean. It has been shown from isotopic studies (Stouraiti *et al.*, 1998; Altherr *et al.*, 1988; Satir *et al.*, 1986) that the granitoids of the eastern Aegean have a higher proportion of enriched mantle component relative to the western arc magmatic rocks, as a result of this different tectonic regime. It is suggested that this is associated with a rather specific tectonic setting in the broad eastern Aegean area, including Kos-Samos-Patmos-Chios and Bodrum, in a zone extending broadly in a N–S orientation, that is transverse to the modern volcanic arc.

Manganese-rich garnets crystallize from magmas enriched in volatile constituents (Baldwin and von Knorring, 1983; Bogoch *et al.*, 1997). According to Green (1977), spessartine-rich garnets in rocks of granitoid composition show evidence of formation at low *P-T*. In granites (Bogoch *et al.*, 1997), the almandine-spessartine magmatic garnets are commonly zoned either with increasing Fe relative to Mn from core to rime or *vice versa*, depending on the nature of the granitic magma and the crystallization conditions. The composition of the almandine-spessartine garnets in pegmatites and aplites is more stable not showing any significant zoning.

In the Profitis Ilias rhyolite, zinnwaldite crystals coexist with spessartine-rich garnets. It is clear that both zinnwaldite and spessartine-rich garnet can be generated as primary phases from a granite melt enriched in volatile constituents at low *P-T* of formation. That rhyolitic magma could represent the residual liquid enriched in volatile constituents associated with a (currently) unexposed A-type granite in the eastern Aegean area.

Henderson *et al.* (1989), reviewing the experimental work on the stability of Li-micas, showed that granite melts highly enriched in F, Li, Rb, Cs (and B) could exist at temperatures down to ~500–550°C and 1 kbar P_{fluid}. From such a granite melt, enriched in volatile constituents, zinnwaldite crystals can be formed as primary phases. Stone (1992) working on the petrogenesis of Li-mica granites in the Cornubian batholith suggests that all the petrogenetic models imply the generation of Li-mica granite magmas after the biotite granites. The volatile constituents required can be generated from a subcrustal (mantle or crust/mantle interface) source above an active mantle. Stone *et al.* (1997) suggested that one way of generating Li–mica granites would be by partial fusion of earlier granite residues, in which case the garnet–zinnwaldite phenocrysts association would be easily explicable. That is provided that there is sufficient heat in the granite-generating system to melt residues from an earlier formed granite (but see Creaser *et al.*, 1991). However, Taylor and Fallick (1997) point out that those granites that have high concentrations of Li, Nb, Ta, etc., are also very rich in F, which has the effect of reducing the viscosity of such liquids so that they could be "erupted as lava flows or tuffs".

It is well known that the Aegean Sea is one of the most rapidly extending areas of continental crust in the world (Angelier *et al.*, 1982). The extensive and deep faulting in the broad eastern Aegean lithosphere section would have facilitated the rapid ascent of that granite melt, enriched in volatile constituents, to act as a parent to the Profitis Ilias rhyolite.

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