Primary allanite in andesitic rocks from the Poros Volcano, Greece

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Abstract

Primary allanite crystals occurring in andesitic rocks from Poros, NE Peloponnese, Greece were studied. Although the allanite shows high *REE* content, its presence does not affect the whole-rock *REE* content of the andesite. It is suggested that the formation of allanite crystals reflects the crystallization history of the andesitic rocks where allanite occurs. These andesitic rocks are the most basic rocks in which allanite has been reported.

KEYWORDS: allanite, andesitic rocks, rare earth elements, Poros, Greece.

Introduction

ALLANITE, a member of the epidote group, has been reported as a common accessory mineral in many granitic rocks and pegmatites (Deer *et al.*, 1962). Although allanite is considered as a rather rare mineral in volcanic rocks, it has been found in trace amounts in ash-fall and ash-flow tuffs (Izett and Wilcox, 1968), as phenocrystic allanite in porphyritic rhyolites (Branch, 1966; Duggan, 1976; Hildreth, 1979) and in obsidian (Cameron and Sabine, 1969; Sabine, 1970; Brooks *et al.*, 1981).

In the course of studying the geochemistry of the volcanic rocks of the Aegean island arc, crystals of primary allanite were found in andesitic rocks from Poros. These rocks seem to be the most basic rocks in which primary allanite has been reported.

Geological setting

Poros, a peninsula on the NE Peloponnese, is one of the major volcanic centres of the Aegean island arc. The Cainozoic volcanic rocks of Poros range in composition from dacite to andesite. Samples from three slightly different types of andesite from Poros were analysed for major and trace elements by X-ray fluorescence analysis at the Department of Geology of the University of Leicester and by instrumental neutron activation analysis at the Nuclear Research Center of Greece 'Democritos'. Details on the analytical procedure, precision and accuracy of the analytical techniques are given in Marsh *et al.* (1983) and Weaver *et al.* (1983) for the XRF and in Grimanis *et al.* (1977, 1980) for the INAA. The chemical compositions of the analysed andesitic rocks along with their CIPW norms are given in Table 1.

The andesitic rocks of Poros show calc–alkaline geochemical characteristics. They show *REE* patterns with *LREE* enrichment (Fig. 1) and their mantle normalized diagrams (Fig. 2) show LIL-element enrichment relative to the high field strength (HFS) elements. Further details on the geochemistry of the Poros volcanic rocks are given in Mitropoulos *et al.* (1986).

Mineralogy of the andesites from Poros

The mineralogy of the andesitic rocks from Poros has been investigated by microscopic and electon-microprobe analyses. Mineral analyses were made on a Cambridge Scientific Instruments Microscan 5 electron probe in the Department of Geology at the University of Leicester, using either wavelength- or energy-dispersive methods. In both cases the standards used were of pure elements or natural compounds. The mineralogical constituents of each of the analysed andesites are given in Table 2.

As it is shown in Table 2, allanite crystals only occur in andesite PO-2 which is free of olivine and clinopyroxene crystals. Olivine and clinopyroxene crystals are present in andesites PO-1 and PO-3 where no allanite occurs. The fine-grained groundmass of the three andesitic rocks PO-1, PO-2 and PO-3 was checked by wavelength-dispersive electron-microprobe qualitative analysis

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TABLE 1. Chemical compositions and CIPW norms of andesites from Poros

Sample no.	PO-1	PO-2	PO-3
SiO_2	62.17	61.79	61.70
TiO_2	0.43	0.44	0.45
Al_2O_3	17.39	17.40	17.72
Fe_2O_3	3.93	2.97	2.47
FeO	0.38	1.40	1.92
MnO	0.11	0.10	0.11
MgO	2.71	2.83	2.98
CaO	6.16	6.22	6.62
Na_2O	3.36	3.31	3.50
K_2O	2.30	2.24	2.09
P_2O_5	0.12	0.13	0.13
LOI	0.71	0.97	0.78
Total	99.77	99.80	100.47
Nb	9.3	9.1	8.6
Zr	123.8	133.5	132.3
Y	13.8	15.6	14.1
Sr	353.4	362.4	381.2
Rb	106.8	105.4	104.2
Th	12.0	12.9	14.0
Ba	378.2	405.7	404.3
Hf	3.20	3.50	3.86
La	21.5	25.9	30.7
Ce	40.1	47.3	54.2
Nd	16.6	19.3	20.7
Sm	2.88	3.25	3.62
Eu	0.76	0.88	1.00
Gd	3.86	4.31	4.85
Tb	0.76	0.81	0.90
Tm	0.40	0.45	0.50
Yb	2.20	2.54	2.82
Lu	0.32	0.37	0.41
CIPW norm			
Qtz	17.38	17.47	15.64
Or	13.58	13.26	12.38
Ab	28.40	27.99	29.64
An	25.60	26.01	26.45
Di	4.94	3.77	5.03
Hy	4.46	5.31	5.99
Mt	-	3.58	3.59
Ilm	1.04	0.83	0.85
Hm	3.93	0.50	-
Ap	0.28	0.30	0.30
Total	99.61	99.02	99.87

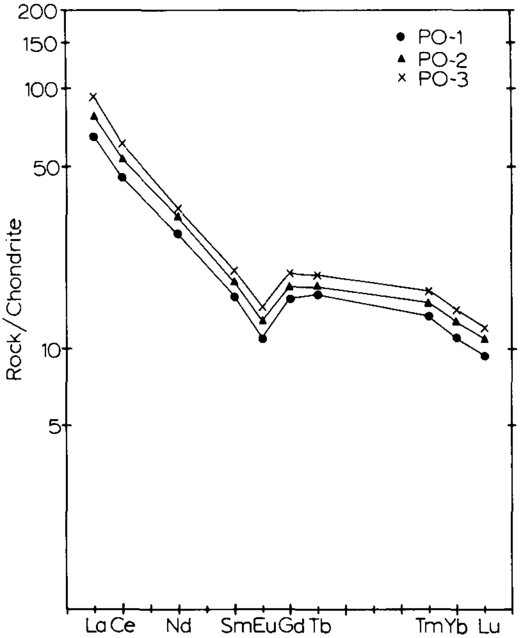

FIG. 1. Whole-rock *REE* patterns of the andesites from Poros.

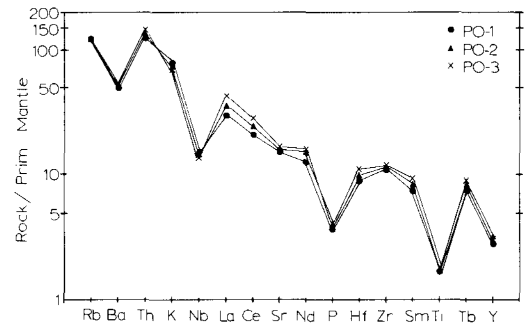

FIG. 2. Primordial mantle normalized diagrams of the andesitic rocks from Poros.

for allanite. Although allanite microcrystals have been pointed out in the groundmass of andesite PO-2 no allanite microcrystals were found in andesites PO-1 and PO-3. The groundmass of andesites PO-1 and PO-3 (separated by hand-picking) was also analysed by XRD but no allanite was found.

Allanite occurs in andesite PO-2 as hypidiomorphic, discrete grains in the glass, up to 2 mm in length, not showing any obvious association to other minerals. In thin section allanite is pale greenish brown, slightly anisotropic, showing no cleavage, alteration or zoning (Fig. 3). The mean chemical composition (20 analyses) of allanite and representative analyses of the other mineralogical constituents of the andesite PO-2 are given in Tables 3*a* and *b* respectively. No significant compositional variation of the allanite crystals has been observed by microprobe analysis.

Discussion and conclusions

The allanite crystals of the andesite PO-2 from Poros contain 8.66% Ce_2O_3 and 4.22% La_2O_3

TABLE 2.

Mineral constituents of the analysed andesites from Poros

Sample no.	PO-1	PO-2	PO-3
Plagioclase	+	+	+
Amphibole	+	+	+
Olivine	+	-	+
Clinopyroxene	+	-	+
Biotite	+	+	-
Magnetite	+	+	+
Apatite	-	-	+
Allanite	-	+	-

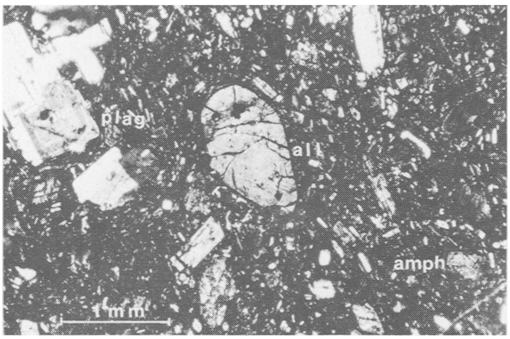

FIG. 3. Photomicrograph of primary allanite phenocryst in glass from andesite PO-2 from Poros (Nic. +).

(Table 3*a*), amounts which are considerably lower than those reported in the literature for allanites occurring in granitic and acid volcanic rocks. Ca occupies about 72% of the *A*1 and *A*2 sites in the structure, which means that there is about 55% occupancy of the *A*2 sites by *REE* as they are partitioned almost entirely into the larger *A*2 sites (Dollase, 1971). The substitution of Ca by *REE* is considerably lower in the allanite crystals of the andesite from Poros than that usually found in allanites from granites and pegmatites, which commonly have up to 90% occupancy of *A*2 sites by *REE*. That can be attributed to the lower *REE* content of an andesitic magma relative to that of the granitic magmas.

REE substitution for Ca in the allanite structure is accompanied by the charge balancing presence of Fe^{2+} in addition to Al^{3+} and Fe^{3+} in octahedral sites (Dollase, 1971; Morin, 1977).

TABLE 3a Mean chemical composition (20 analyses) of allanite andesite PO-2

		12.5 (0)		
SiO_2	32.97	Si	3.00	
Al_2O_3	16.76	Al	1.80	
Fe_2O_3 *	8.33	Fe^{3+}	0.57	2.98
FeO *	6.08	Fe^{2+}	0.47	
MgO	0.98	Mg	0.14	
CaO	14.83	Ca	1.44	
La_2O_3	4.42	La	0.15	
Ce_2O_3	8.66	Ce	0.28	
Nd_2O_3	2.63	Nd	0.08	2.03
Pr_2O_3	0.86	Pr	0.03	
Y_2O_3	0.47	Y	0.02	
ThO_2	1.35	Th	0.03	
H_2O **	(1.63)	OH	(1.00)	
Total	99.97			

* oxidation state calculated assuming stoichiometry of 8 cations and 12.5 oxygens per formula unit

** calculated % H_2O has been inserted on the assumption of one (OH) per formula unit of the type $(Ca, REE)_2(Al, Fe^{3+}, Fe^{2+})_3Si_3O_{12}(OH)$

TABLE 3b Representative analyses of the mineral constituents of andesite PO-2.

	Plagiocl.	Amphibole		Biotite		Magnetite
SiO_2	57.49	43.03		37.44		0.40
TiO_2	-	0.86		2.98		4.24
Al_2O_3	27.17	10.08		15.99		2.12
FeO*	-	16.28		18.21		89.14
MgO	-	11.35		12.44		1.14
MnO	-	0.64		0.37		0.75
CaO	9.59	11.45		-		-
Na_2O	5.68	1.26		0.93		-
K_2O	0.33	0.68		8.68		-
Total	100.26	95.63		97.04		97.79
	8(0)	23(0)		22(0)		32(0)
Si	2.564	6.583	8.00	5.550	8.00	0.147
Al^{VI}	1.429	1.417		2.450		0.906
Al^{IV}		0.400		0.344		
Ti	-	0.099		0.332		1.155
Fe^{2+}	-	2.083	5.25	2.258	5.73	27.011
Mg	-	2.587		2.748		0.614
Mn	-	0.083		0.046		0.230
Ca	0.459	1.877		-		-
Na	0.492	0.373	2.38	0.268	1.91	-
K	0.019	0.132		1.642		-

* total iron as FeO

The analysed andesitic rocks from Poros show small differences in their chemical and normative compositions (Table 1), similar mantle normalized diagrams (Fig. 2) and similar whole-rock *REE* patterns in spite of the absence of any allanite crystals (pheno- or micro-) in the andesites

PO-1 and PO-3. The three andesitic rocks do not show any increased *REE* content as compared either to andesitic rocks from other volcanic centres of the Aegean island arc (Mitropoulos *et al.*, 1986) or to andesitic rocks from other calc-alcaline volcanic series (e.g. Cole *et al.*, 1983).

Accessory minerals may contain a high proportion of whole-rock *REE* and may exert control on the *REE* pattern of an igneous rock if they are involved in fractional crystallization or partial melting processes during magma generation. Exley (1980) working on *REE*-rich accessory minerals from Skye granite suggested that allanite may contain up to 50% of whole-rock *LREE*. The high *REE* content of allanite relative to the whole-rock *REE* content of the andesite PO-2 implies that the large proportion of the whole-rock *REE* may have resided in the allanite crystals. In andesites PO-1 and PO-3 where no allanite occurs, the *REE* may have entered into the structures of the amphibole and the biotite, minerals with suitable structural sites to accommodate the large *REE* cations. Gromet and Silver (1983) suggested that the abundance of allanite in granodioritic rocks principally reflects variation in melt composition and the intensive variables that govern crystallization. In the present case, taking into account the similar chemical compositions of the three andesitic rocks from Poros, it can be suggested that the formation of primary allanite crystals in andesite PO-2 and the absence of olivine and clinopyroxene crystals reflects a different crystallization history than those of andesites PO-1 and PO-3. Furthermore the bulk rock system of andesite PO-2 may have remained closed throughout its crystallization.

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References

Branch, C. D. (1966) Volcanic couldrons, ring complexes and associated granites of the Georgetown inlier, Queensland. *Bull. Bur. Mineral. Resour. Geol. Geophys. Austral.* **76,** 1558–67.

Brooks, C. K., Henderson, P. and Rønsbo, J. G. (1981) Rare earth partition between allanite and glass in the obsidian of Sandy Braes, Northern Ireland. *Mineral. Mag.* **44,** 157–60.

Cameron, I. B. and Sabine, P. A. (1969) The tertiary welded-tuff vent agglomerate and associated rocks at Sandy Braes Co. Antrim. *Rep. Inst. Geol. Sci.* 69/6, 15 pp.

Cole, J. W., Cashman, K. V. and Rankin, P. C. (1983) Rare-earth element geochemistry and the origin of andesites and basalts of the Taupo Volcanic Zone, New Zealand. *Chem. Geol.* **38,** 255–74.

Deer, W. A., Howie, R. A. and Zussman, J. (1962) *Rock forming minerals* **1,** *Ortho and ring silicates.* Longmans, London, 333 pp.

Dollase, W. A. (1971) Refinement of the crystal structures of epidote, allanite and hancockite. *Am. Mineral.* **56,** 447–64.

Duggan, M. B. (1976) Primary allanite in vitrophyric rhyolites from the Tweed Sield volcano, north-eastern New South Wales. *Mineral. Mag.* **40,** 652–3.

Exley, R. A. (1980) Microprobe studies of *REE*-rich accessory minerals: implications for Skye granite petrogenesis and *REE* mobility in hydrothermal systems. *Earth Planet. Sci. Lett.* **48,** 97–110.

Grimanis, A. P., Vassilaki-Grimani, M. and Griggs, C. B. (1977) Polution studies on trace elements in sediments from the upper Saronikos Gulf, Greece. *J. Radioanal. Chem.* **37,** 761–73.

—— Filippakis, S. E., Perdikatsis, B., Vassilaki-Grimani, M., Bosana-Kourou, N. and Yalouris, N. (1980) Neutron activation and X-ray analysis on 'Thapsos Class' vases. An attempt to identify their origin. *J. Archaeolog. Sci.* **7,** 227–39.

Gromet, L. P. and Silver, L. T. (1983) Rare earth element distributions among minerals in a granodiorite and their petrogenetic implications. *Geochim. Cosmochim. Acta* **47,** 925–41.

Hildreth, W. (1979) In *Ash-flow tuffs* (Chapin, C. E. and Elston, W. E., eds.) Spec. Pap. Geol. Soc. Am. **180,** 43–75.

Izett, G. A. and Wilcox, R. E. (1968) Perrierite, chevkinite and allanite in upper Cenozoic ash beds in the western United States. *Am. Mineral.* **53,** 1558–67.

Marsh, N. G., Tarney, J. and Hendry, G. L. (1983) Trace element geochemistry of basalts from Hole 504B, Panama Basin, DSDP Legs 69 and 70. *Init. Repts DSDP 69*, 747–64 (Washington: U.S. Govt. Printing Office).

Mitropoulos, P., Tarney, J., Saunders, A. D. and Marsh, N. G. (1986) Petrogenesis of Cenozoic volcanic rocks from the Aegean island arc. *J. Volc. Geotherm. Res.* (in press).

Morin, J. A. (1977) Allanite in granitic rocks of the Kenora–Vermilion Bay area northwestern Ontario. *Can. Mineral.* **15,** 297–302.

Sabine, P. A. (1970) Perlitic obsidian at Sandy Braes Co. Antrim: its devitrification and volumetric relationships. *Rep. Inst. Geol. Sci.* 70/11, 8 pp.

Weaver, B. L., Marsh, N. G. and Tarney, J. (1983) Trace element geochemistry of basaltic rocks recovered at site 516, Rio Grande Rise, DSDP Leg 72. *Init. Repts. DSDP 72*, 451–6 (Washington: U.S. Govt. Printing Office).

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