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NON-METAMICT ALLANITE FROM SERIFOS ISLAND, CYCLADES (GREECE)

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ABSTRACT

Non-metamict allanite from the skarn on Serifos island Cyclades /Greece was studied opticaly, by X-ray diffraction - and microprobe analysis. The allanito is associated mainly with andradite as well as with epidote - albite. The mineral formula according to microprobe analysis is :

$(Ca_{1.427}La_{0.327}Ce_{0.287}Pr_{0.01}Nd_{0.023})_{2.07}(Al_{1.87}Fe^{3+}_{0.131})$
$(Fe^{2+}_{0.552}Fe^{3+}_{0.232}Mg_{0.063}Mn_{0.016})_{0.87}Si_{3.04}O_{12.5}$

The lattice parameters are :a_o=8.905(1) A, b_o=5.699(1) A, c_o=10.131(2) A, β=114.97°. density= 3.772g/cm³.

The crystal structure of allanite was refined by the "Rietveld" method and compared with that from literature.

Optical properties: nα=1.750, light brown, nβ=1.760, dark brown, nγ=1.776, dark brownish-red. 2Vα=60°, nα^c=44°, O.A.P \\(010).

Keywords:Allanite,Serifos/Greece, skarn, x-ray diffraction, "Rietveld" analysis, microanalysis.

INTRODUCTION

The island of Serifos is situated about 100 km SSE of Athens, in the western part of the central Aegean Sea , (fig.1).

Geologically it belongs to the Attic-Cycladic unit of the Pelagonian massif (fig.1) and consists , as a part of a median crystalline belt within the Alpine orogenic chain of the Hellenides, mainly of metamorphic rocks recording at least three different metamorphic events (DUERR et al. 1978).

1.(M1):Glaucophane schist facies, regional metamorphism, dated at 45-50 Ma (ALTHERR et al., 1979).

2.(M2):Greenschist facies, regional metamorphism, dated at 25-30 Ma (ALTHERR et al., 1982).

3.(M3):Low pressure contact metamorphism, associated with local granitoid plutonism, dated at about 10 Ma (DUERR et al.,1978).

Granitic intrusion (finegrained biotite - hornblende-

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granodiorite, I-type) caused the formation of hornfels and the skarnification of the already metamorphosed (M1+M2) basement. These rocks represent the M3 metamorphic phase.

Metasomatic phenomena are widespread on the island, along the northern as well as the southern granodiorite-basement contact, several kilometers long, up to 1000 m wide and 100 m thick (fig.2).

Lime-, magnesian- and silicate skarn are present, with the conditions of infiltration during the metasomatic processes, being the most common.

Massive skarn has been formed mainly in the central and the western part of the island, showing an unusual mineral growth and distinctive metasomatic zonation, which includes Fe-ore deposits (magnetite, hematite, limonite) and minor Cu, Pb-Zn and F-Ba mineralizations (PAPASTAVROU & ZOGRAFOU ,1979), (PAPASTAVROU & PERDIKATSIS (1990).

In several skarn bodies allanite occurs mainly concentrated in the southern part of skarn (fig. 2). This allanite skarn body has an approximately 1-20 m thickness, 60-80 m width and 150 m length .

The allanite participates in the rock with 1-3 vol. %. In the field can be located easily with a scintillation counter, due to its content in radioactive elements (Th,, U).

DESCRIPTION OF THE MATERIAL

The allanite appears in two forms: (a) As a rock component in association with andradite, epidote, hedenbergite, albite and (b) filling veins in association with epidote, ± andradite, quartz, ± magnetite, diopside, ± albite. In the first case it is fine or coarse grained, up to 5 cm (fig. 3). The veins crosscut the allanite bearing garnetite.

Allanite commonly shows varying degree of metamictization due to the content in radioactive elements in its structure. Well crystallized allanite is rather uncommon. On the contrary the allanite of Serifos is very well crystallized (non- metamict), with extensive pleochroic haloes developed in large allanite grains.

The refractive indices for green light were determined using the immersion method: $n\alpha=1.750$, $n\beta=1.760$, $n\gamma=1.776$, $2V\alpha=60°\pm5$. Pleochroism is strong :$n\alpha$=light brown, $n\beta$=dark brown, $n\gamma$=dark brownish- red. Absorption for $n\beta$ and $n\gamma$ is also very strong. The single crystal grains are hypidiomorphic and twinning along (100) is frequent. The optic axial plane is parallel to (010) and the extinction angle between $n\omega$ and c-axis was determined to be $n\alpha$^c=about 44°. The optical properties of the Serifos allanite are in acordance with those of literature (TROEGER, 1969), (DEER, et al. 1962).

Density determined at single grains gave D=3.772 g/cm³ with grains up to 200 mg.

X-RAY DIFFRACTION

The X-ray diffraction analysis was used in order to determine the lattice parameters. A fully automated X-ray powder diffraction system from SIEMENS D500, with copper tube was used for the X-ray diffractograms. Scannings were made at 40 KV and 30 mA with 0.02° step and 4 sec. counting time, using 1° slits and secondary graphite Monochromator.

In order to detect probable metamictization in the studied allanite, diffractograms were carried out after 5h heating at 500° C, 600° and 700° C. Differences were not observed, neither in d values nor in intensities and in full-width at half-maximum. This indicates that metamictization does not exist, and allanite is well crystallized as it has been proved by the microscopic observation

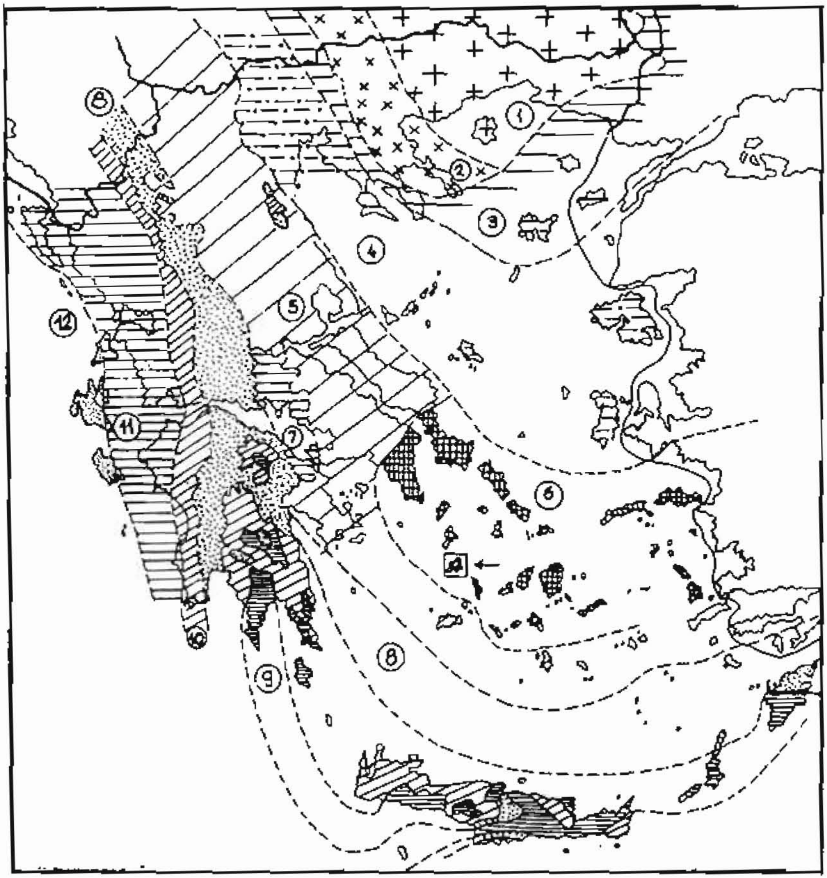

Figure (1). Geographic position of Serifos island and distribution of the geotectonic units in Greece.
1. Rhodope zone 2. Perirhodope zone 3. Serbomacedonian zone
4. Axios zone 5. Pelagonian massif 6. Attic-Cyclades massif
7. Parnassos-Giona zone 8. Pindos zone 9. Tripolis zone
10. Gavrovo zone 11. Ionian zone 12. Paxos zone.

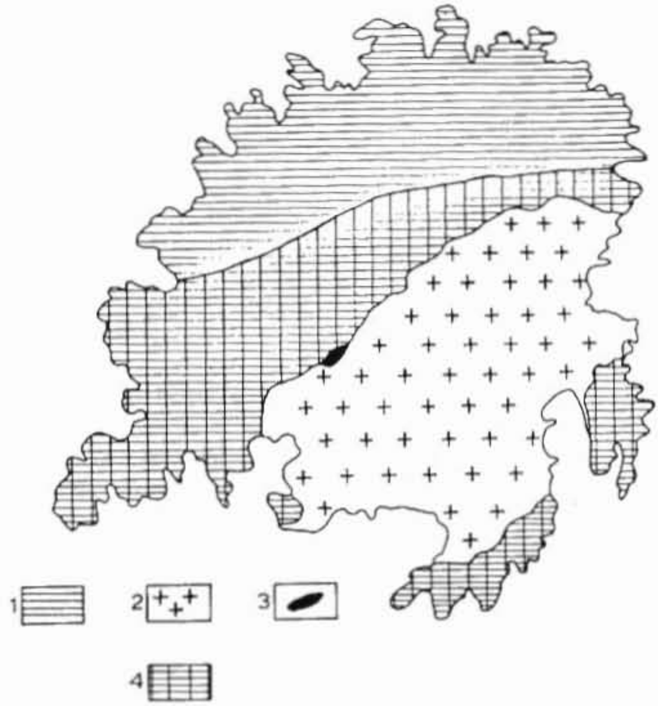

Figure (2). Geological map of Serifos island (simplified).
1. Metamorphic basement. 2. Granodiorite
3. Allanite occurence. 4. Metasomatosed basement

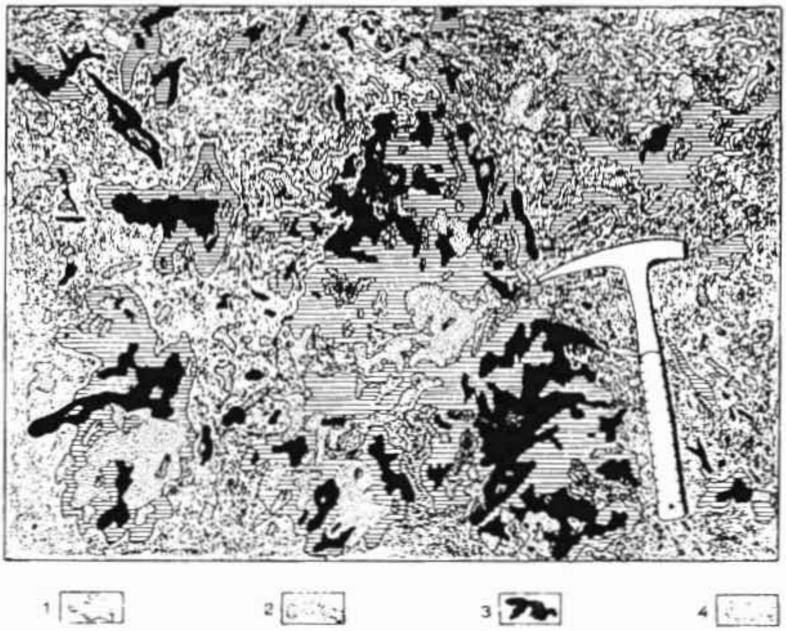

Figure (3). Distribution of allanite and coexisting minerals.

as well. Decomposition of allanite as reported by VANCE & ROUTCLIFFE (1976), for metamict material was not observed.

The crystal structure of allanite was refined by the "Rietveld" method using the program of BISH & HOWARD (1988).

Allanite is the only member of the epidote group in which Fe^{2+} (ferrous iron) is an essential component. The ferrous iron replaces Al and there is a balancing substitution of Ca by REE such as Ce and La.

The initial structure model for the "Rietveld" refinement was thus from DOLLASE (1971). According to him allanite is isotype with epidote. The crystal structure contains two large sites, A(1) and A(2), which are usually occupied by Ca, three tetrahedral sites occupied only by Si, and three octahedral coordinated sites M(1), M(2), M(3), principally occupied by cations of charge +3 such as Al, Fe^{3+}. This gives rise to the formula:

$Ca_2M^{3+}{}_3Si_3O_{11}O(OH)$.

In allanite structure REE (rare earth elements) are ordered in A(2) with charge balance maintained by substitution of Fe^{2+} for Fe^{+3}, principally in site M(3) . This position contains also small quantities of Th, U, Na, Y and Mn. In addition there is a significant substitution of Fe^{3+} for Al.

The results of the Rietveld crystal structure refinement is given in table 1 and figure(4) . According to this study the "Rietveld" refinement confirmed the above structure. A(1) site is occupied 99% by Ca and 1% bei REE . A(2) is occupied 49% by REE and 51% by Ca. M(1) is occupied 72.4% by Al and 27.6% by Fe while M(3) 27% by Al and 73% by Fe. M(2) contains only Al. The value of Al in M(1) is equal to that of Fe in M(3) and the value of Fe in M(1) is equal to that of Al in M(3).

According to "Rietveld" fitting the crystal formula of allanite can be written as: $Ca_{1.5}REE_{0.5}FeAl_2Si_3O_{12}OH$.

The lattice constants as well as the d-values are in accordance with the corresponding values given by FRANTISEC & PAVEL (1972), DOLLASE (1971), PEACOR & DUNN (1988).

THERMAL ANALYSIS

The thermal behaviour of allanite was studied by a Mettler thermoanalyser. A strong endothermic reaction appears at 960° C associated with a loss of 1.4 % H_2O. Other reactions as reported by FRANTISEC & PAVEL (1972) were not observed in the present study.

CRYSTAL CHEMISTRY

The chemical composition of allanite was determined by electron microprobe in polished and carbon coated thinsections. An automated Jeol Superprobe 733 microanalyser was used, using synthetic- and mineral-standards for Z A F corrections. The operating conditions for the measurements were: accelerating potential 20 KV, beam current 8 nA and 20 sec counting time for peak and background. Beam diameter was 1 μm. Analyses of allanites are given in table (2).

Because iron is determined by electron microprobe either as FeO or Fe_2O_3, different ways can be used to calculate the mineral formula of allanite:

A. Anhydrous formula for 12.5 oxygen
B. Formula for 13 oxygens including H2O+.
For every case the following calculations are possible:
1. Calculation for Fe^{2+}-total
2. Fe^{2+}/Fe^{3+} distribution for Si=3
3. Calculation of oxygen number for Si=3 and Fe^{2+}-total.
4. Fe^{2+}/Fe^{3+} distribution for Σ cations = 8.
5. Fe^{2+}/Fe^{3+} distribution for A(1)+A(2)+M(1)+M(2)+M(3)=5.

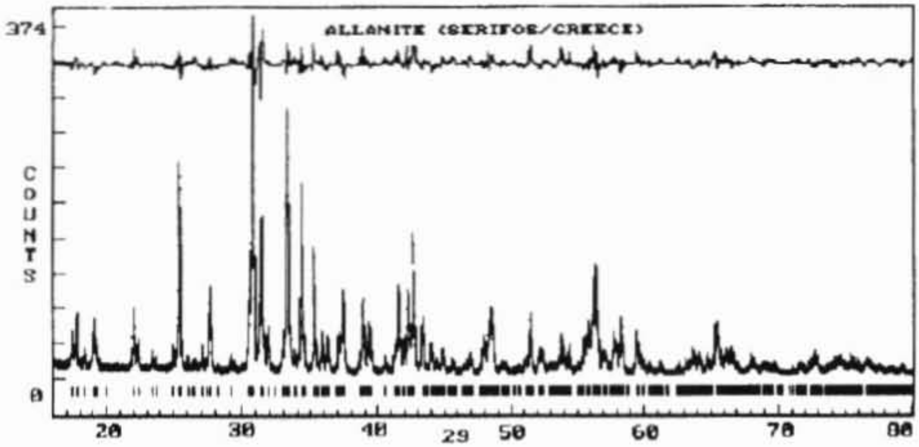

Figure (4). Observed and calculated patterns for Allanite from Serifos after "Rietveld" refinement.
The curve shows the difference between the observed and calculated patterns. Vertical marks at the botton indicate the position of allowed Ka1 and Ka2 lines.

Table (1). Results of structure refinement of Allanite after the "Rietveld" method.

Space Group: $P\ 2_1/M$

ao (A)	bo (A)	co (A)	β (°)
8.905(1)	5.699(1)	10.131(2)	114.97(2)

Density (gr/cm^3): 3.79 Cell Volume (A^3): 466.06 Z=2

R:13.59% R w =15.04% R exp.=4.36% R Bragg =9.65%

ASYM.F.	Mo	M1	U	V	W
0.18006	-0.10441	0.02694	1.0169	1.1079	0.0037

Position	Atom	X	Y	Z	B	Occup.
A(1)	Ca	0.7516(8)	0.7500	0.1500	0.70	0.496(3)
A(1)	Ce	0.7516(8)	0.7500	0.1500	0.70	0.004(3)
A(2)	Ce	0.5939(9)	0.7500	0.4275(7)	0.70	0.246(4)
A(2)	Ca	0.5939(9)	0.7500	0.4275(7)	0.70	0.254(4)
SI(1)	Si	0.3354(9)	0.7500	0.0377(8)	0.70	0.500
SI(2)	Si	0.6829(8)	0.2500	0.2702(8)	0.70	0.500
SI(3)	Si	0.1817(9)	0.7500	0.3286(9)	0.60	0.500
M(1)	Al	0.0000	0.0000	0.0000	0.60	0.362(9)
M(1)	Fe	0.0000	0.0000	0.0000	0.60	0.138(9)
M(2)	Al	0.0000	0.0000	0.5000	0.60	0.500
M(3)	Fe	0.2953(8)	0.2500	0.2155(8)	0.90	0.365(9)
M(3)	Al	0.2953(8)	0.2500	0.2155(8)	0.90	0.135(9)
O(1)	O	0.2531(8)	0.9889(8)	0.0342(8)	1.30	1.000
O(2)	O	0.3040(8)	0.9788(8)	0.3569(8)	1.10	1.000
O(3)	O	0.7713(9)	0.0155(7)	0.3285(8)	1.00	1.000
O(4)	O	0.0696(8)	0.2500	0.1451(7)	1.20	0.500
O(5)	O	0.0496(8)	0.7500	0.1378(7)	1.20	0.500
O(6)	O	0.0709(8)	0.7500	0.4066(8)	0.90	0.500
O(7)	O	0.5019(8)	0.7500	0.1794(8)	1.00	0.500
O(8)	O	0.5368(8)	0.2500	0.3445(8)	1.50	0.500
O(9)	O	0.6372(9)	0.2500	0.1106(8)	1.70	0.500
O(10)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.500

Chemical formula after the structure refinement:
Ca REE FeAl Si O OH

Table (2). Microprobe analyses of allanite from Serifos (Greece).

	A (N=10)		B (N=7)		C (N=7)		D (N=3)		E (N=6)		
	c %	cation	c %	cation	c %	cation	c %	cation	c %	cation	
SiO_2	33.74	3.040	33.63	3.000	34.53	2.996	34.33	2.924	33.73	3.008	Si
Al_2O_3	17.58	1.870	18.90	1.987	19.57	2.001	19.80	1.988	17.80	1.872	Al
FeO	12.24	0.552	12.54	0.501	12.51	0.361	15.63	0.259	13.89	0.475	Fe^{2+}
Fe_2O_3		0.372		0.440		0.547		0.854		0.561	Fe^{3+}
MgO	0.47	0.063	0.48	0.064	0.52	0.067	0.25	0.032	0.44	0.058	Mg
CaO	14.76	1.427	15.08	1.442	16.91	1.572	17.70	1.614	15.40	1.472	Ca
TiO_2	0.17	0.011	0.08	0.005	0.21	0.014	0.27	0.018	0.07	0.005	Ti
MnO	0.22	0.016	-	-	0.15	0.011	0.51	0.037	0.12	0.009	Mn
La_2O_3	9.63	0.320	8.23	0.271	7.44	0.238	3.87	0.122	8.35	0.275	La
Ce_2O_3	8.69	0.287	7.89	0.258	5.09	0.162	4.36	0.136	7.31	0.239	Ce
Pr_2O_3	0.30	0.010	0.31	0.010	0.32	0.010	0.17	0.005	0.28	0.009	Pr
Nd_2O_3	0.71	0.023	0.62	0.020	0.64	0.020	0.31	0.009	0.47	0.015	Nd
ThO_2	0.10	0.002	0.10	0.002	0.10	0.002	0.05	0.001	0.09	0.002	Th
UO_2	0.01										U
ΣCa,REE		2.07		2.003		2.004		1.888		2.012	
ΣAl,Fe,Mg,Mn		2.885		2.997		3		3.188		2.980	
Σ cations		8		8		8		8		8	
Oxygens		12.5		12.5		12.5		12.5		12.5	

The chemical formula of allanite was calculated using the computer program for mineral formula calculation of PERDIKATSIS (1986).

Because H_2O+ is not direct determined by the analysis, we discuss only the formulas for 12.5 oxygens.

The number of REE^{3+} cations is independent from the type of the formula calculation.

Ca shows a small variation and Fe^{2+}/Fe^{3+} is strongly dependent from the way of calculation.

Wet chemical analysies of FeO and Fe_2O_3 are close to the values which are taken for case 4 of calculation . In this case the sum of cations are defined to be 8. The computer programme calculates first the cation charge for FeO-total and balances the difference, from 25 total cation charge for 12.5 oxygens, converting a part of FeO-total to Fe_2O_3 .

Table (2) gives composition and formulas for allanites of Serifos, calculated in the above way.

According to table (2) the sum of the REE varies from 19.33% to 13.49%. The La/Ce ratio varies from 0.9 up to 1.46. The FeO-total values are constant except sample D and E. Al_2O_3 varies inverse to the sum of REE.

The allanite formula for the analysed crystals are:

A.-$[Ca_{1.427}La_{0.32}Ce_{0.287}Pr_{0.01}Nd_{0.023}]_{2.07}[Al_{1.87}Fe^{3+}{}_{0.13}]_2$

$[Fe^{2+}{}_{0.552}Fe^{3+}{}_{0.232}Mg_{0.063}Mn_{0.016}]_{0.87}Si_{3.05}O_{12.5}$

B.-$[Ca_{1.442}La_{0.271}Ce_{0.258}Pr_{0.01}Nd_{0.02}]_{2.003}[Al_{1.987}Fe^{3+}{}_{0.013}]_2$

$[Fe^{2+}{}_{0.501}Fe^{3+}{}_{0.427}Mg_{0.064}]_{0.992}Si_3O_{12.5}$

C.-$[Ca_{1.572}La_{0.238}Ce_{0.162}Pr_{0.01}Nd_{0.02}]_{2.004}Al_2$

$[Fe^{2+}{}_{0.361}Fe^{3+}{}_{0.547}Mg_{0.067}Mn_{0.011}]_1Si_3O_{12.5}$

D.-$[Ca_{1.614}La_{0.122}Ce_{0.136}Pr_{0.005}Nd_{0.009}]_{1.888}$

$[Al_{1.912}Fe^{3+}{}_{0.088}][Fe^{2+}{}_{0.259}Fe^{3+}{}_{0.766}Mg_{0.03}Mn_{0.037}]_{1.09}Si_{2.924}Al_{0.076}O_{12.5}$

E.-[Ca [illegible]]$_2$

$[Fe^{2+}{}_{0.475}Fe^{3+}{}_{0.433}Mg_{0.058}Mn_{0.009}]_{2.98}Si_{3.008}O_{12.5}$.

The mean allanite formula according to table(2) can be written as: Ca 1.505 atoms, REE 0.49 atoms, Al 1.944 atoms and Fe 0.984 atoms or $(Ca,REE)_{1.995}(Al,Fe)_{2.928}Si_3O_{12.5}$ and is in good agreement with that of the "Rietveld" crystal structure refinement.

RARE EARTHS IN HOST ROCKS

As mentioned above the host rock for the allanite in the skarn of Serifos is mainly garnetite. The rare earth content in andradite, which is the main mineral of garnetite, varies for La: 25 - 70 ppm and for Ce:28 -80 ppm. For coexisting epidotes these values are La:400 ppm, Ce:300 ppm. The higher values in epidotes are explained by the similarity of their structure with that of allanite.

DISCUSSION - RESULTS

The allanite of Serifos Island is formed in a skarn zone of an initial metasomatic stage under high temperature conditions (≈550°C, fluid inclusions in quartz). Metasomatism is caused by the intrusion of an I-Type granodiorite into an already polymetamorphosed sequence.

Allanite occurs, almost exclusively, in a garnetite (>50% andradite) skarn with the modal composition andradite - epidote - hedenbergite - quartz - albite ± magnetite, formed in marbles, near to a marble - metaarkose contact and as endoskarn (vein type in the granodiorite).

The black coloured ,light REE mineral is characteristic and invariably present with crystals up to 5 cm. Moreover in central Serifos a significant allanite concentration in rock (up to 3 %) was located, presenting the first known concentration of "light" REE minerals in the Atticocycladic Massif (ACM) on the Aegean sea and Greece.

The non-metamictic character of the Serifian allanite, as established in this study, is in good accordance with its genetic and spatial relationship to the very young granodiorite of Serifos, which is a part of the large lacolith of the ACM (ALTHERR et al., 1982).

Based on :

a.) The low La, Ce values in the dolomitic marbles (<6-20 ppm) as well as in the "white" gneisses (20-30 ppm).

b.) field evidences, such as,

(i). The location of a vein-type allanite mineralization (allanite - albite - andradite -quartz), crosscutting the granodiorite itself, which is recognized as the REE feeder up to the zone of metasomatic processess (massif andradide skarn)

(ii) The formation temperatures of andradide skarn, which are very close to those of the magnetite mineralization (550°C, fluid inclusions in quartz, SALEMINK 1985).

c.) the evidence, that allanite concentrations in Serifos have been located only in andraditic massif skarn

All the above support, as most probable, the hypothesis that there was a genetic link between the allanite and the granodiorite.

The crystal structure of allanite, refined by "Rietveld" fitting, is the same as that of DOLLASE (1971).The crystal chemistry based on microanalyses is in good agreement with that of the crystal structure refinement.

Based on the results of the technological study the recovery of saleable allanite ranges in very low levels (15-20 %), caused mainly by the similarities in the physical properties of other minerals in the assemblage (epidote, garnet etc.).

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