On Some Accessory Minerals in Upper Paleozoic Granites of the Khrami Crystalline Massif

Tamara Tsutsunava[1]*, Giorgi Beridze[1], Irakli Javakhishvili[1]

Abstract

The Khrami crystalline massif is exposed within the Black Sea – Central Transcaucasian terrane (Georgia). The massif is built up of Precambrian gneiss-migmatite complex, the packet of Middle Paleozoic (?) metasandstones and protrusions of mantle serpentinites; Paleozoic gabbroids; Middle-Upper Paleozoic granitoids and rocks of volcanogenic-sedimentary complexes and Upper Paleozoic quartz-porphyry - granite-porphyry formations. A number of scientists have studied the granitoids of the Khrami crystalline massif, but detailed investigations on some minerals using modern analytical facilities have not been conducted yet. The Late Variscan granitoids of the Khrami massif are represented by biotite-hornblende-allanite-, biotite-microcline- and biotite-garnet-bearing granites and aliaskites. We have studied in detail the accessory minerals - garnet and allanite in the Late Variscan granites of the massif. Their microprobe analysis has been performed. According to the microprobe analysis of the studied garnets, the centre of the crystal is homogeneous, while the peripheral part is zonal. The amount of FeO decreases slightly from the centre to the periphery, while the amount of CaO and MgO significantly decreases; a well-expressed increase in MnO content is recorded. The variation in almandine content is insignificant. The amount of pyrope and grossular drops sharply from the centre to the periphery while the number of spessartine increases. The amount of Al_2O_3 in all varieties of granitoids is similar. In our opinion, the garnet formation occurred in two stages: during the crystallization process of granitic magma and its subsequent post-magmatic stage. The core of the garnet was formed in the magmatic stage, but its periphery - was in the cooling stage of granitic magma. According to the results of the microprobe study of allanite, the same - two stages of their formation have been conducted: during the crystallization process of granitic magma and in its next post-magmatic stage. The genesis of allanite in the biotite-hornblende-allanite-bearing granites of the massif is due to the concentration of REE in the granitic magma and the introduction of calcium by hydrothermal solutions. These allanites belong to the cerium variety with high content of Ce_2O_3, La_2O_3 and Nd_2O_3.

Keywords: Georgia, the Khrami massif, accessory mineral, garnet, allanite.

Introduction

The Khrami crystalline massif is exposed within the Black Sea – Central Transcaucasian terrane in the territory of Georgia [4]. It is a washed-out part of the horst-like uplift of the Artvin-Bolnisi belt. The massif is built up of a Precambrian gneiss-migmatite complex, the packet of Middle Paleozoic (?) allochthonous metasandstones exposed in the complex; protrusions of mantle serpentinites; Paleozoic gabbroids; rocks of Middle-Upper Paleozoic granitoids and volcanogenic-sedimentary complexes and Upper Paleozoic quartz-porphyry – granite-porphyry formations (Fig. 1).

The granitoids of the Khrami crystalline massif has been studied by a number of scientists at different times [7, 16, 17, 11, 13, 14, 8, 9, 5, 1, 2, 3].

The Late Variscan granitoids of the Khrami massif are represented by four varieties: biotite-hornblende-allanite bearing, biotite-microcline bearing and biotite-garnet bearing granites and aliaskites. The mineralogical composition of biotite-microcline bearing granites and alaskites is as follows: quartz, plagioclase, microcline and biotite (in alaskites biotite is a secondary mineral); biotite-garnet bearing granites are represented by quartz, plagioclase, microcline, biotite and garnet; the constituent minerals of biotite-hornblende-allanite granites are quartz, plagioclase, microcline, biotite, hornblende and allanite.

The age of the Late Variscan granitoids of the Khrami crystalline massif is reliably established by the U-Pb LA ICP Ms zircon method. In particular, the data of analysis of 27 points correspond to the interval 321-331±6.0 Ma [6].

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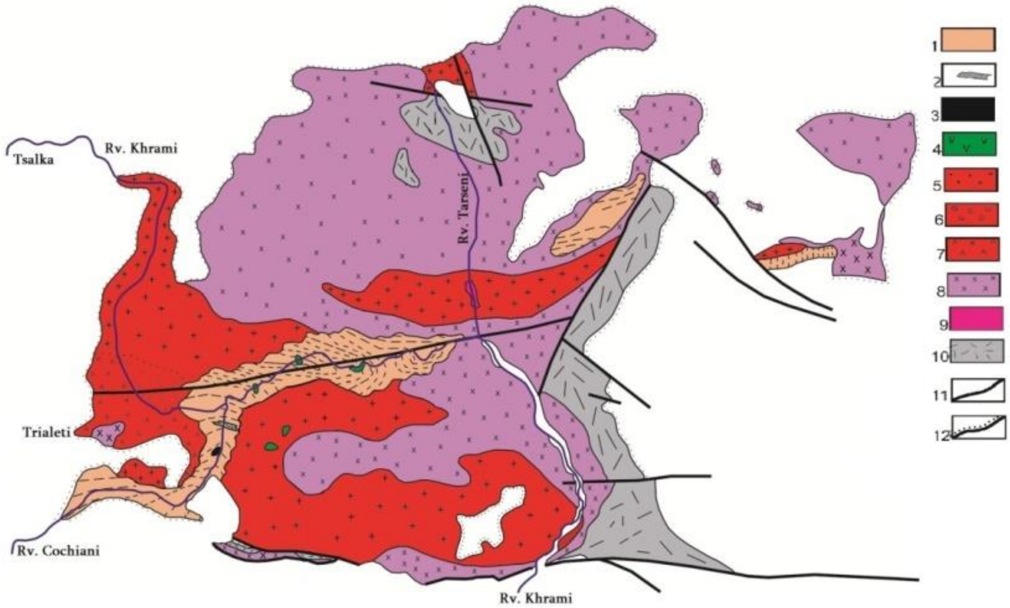

Figure 1. Schematic geological map of the Khrami crystalline massif [6], with G. Beridze additions [3]. 1 – Pre-Cambrian gneiss-migmatite complex; 2 – Middle Paleozoic(?) packet of metasandstones in the gneiss-migmatite complex; 3 – protrusives of mantle serpentinites; 4 – Paleozoic gabbroids; 5-9 – Late Variscan granitoid complex: 5 – biotite-microcline bearing granites and alaskites; 6 – biotite-garnet bearing granites; 7 – biotite-hornblende-allanite bearing granites; 8 - Upper Paleozoic quartz porphyries; 9 – Upper Paleozoic granite porphyries; 10 – Middle-Upper Paleozoic volcanogenic-sedimentary complex; 11 – Mesozoic-Cenozoic sedimentary rocks; 12 – ruptures; 13 – transgressive arrangement.

Methods and Materials

For the determination of minerals composition, a microprobe analysis of garnet and allanite has been carried out. The composition of minerals was determined using an electronic microprobe facility - JEOL JXA-8200, in the laboratory of the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences, in Moscow. The device is equipped with five long-wave dispersive X-ray spectrometers (WDS) and one energy-dispersive X-ray spectrometer (EDS). The analysis was performed with an accelerating voltage of 20 kV, a beam current of 20 nA, and a beam size of 1-2 μm, with a 10-second counting time. All elements were measured along the Ka1 analytical line. See the results of the analysis in Table 1.

Results

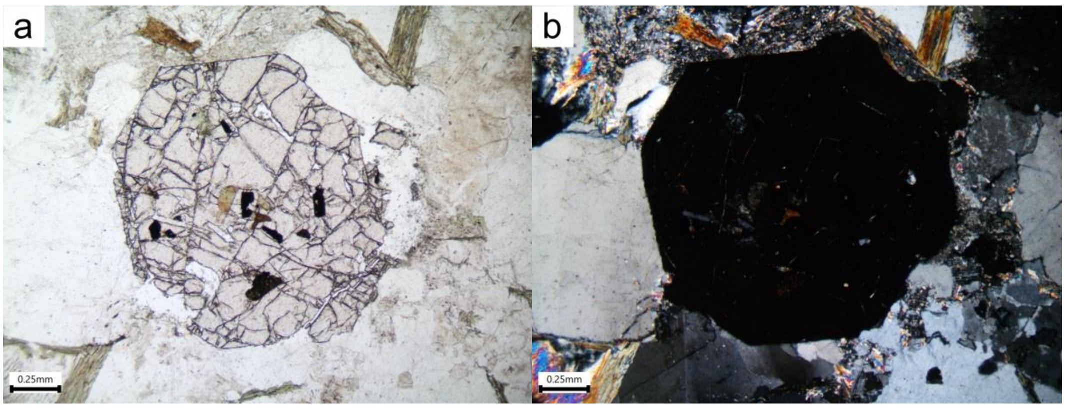

Figure 2. a) Biotite and allanite inclusions in garnet crystal, PPL (plane-polarized light) and b) XPL (cross-polarized light)

We have studied in detail the accessory minerals - garnet and allanite in the late Variscan granites of the Khrami crystalline massif. Within the massif, biotite-garnet bearing granites are exposed in the area of the Khrami Hydroelectric Power Station-I on an area of ≈1-1.5 km2. They are leucocratic, coarse-grained porphyry rocks. The garnet content in the rock is 5-10%. The mineral is presented in the form of well-defined tetragonal-trioctahedral crystals of 2-10 mm size. Garnet grains contain apatite, biotite, zircon and allanite inclusions [11, 13] (Fig. 2).

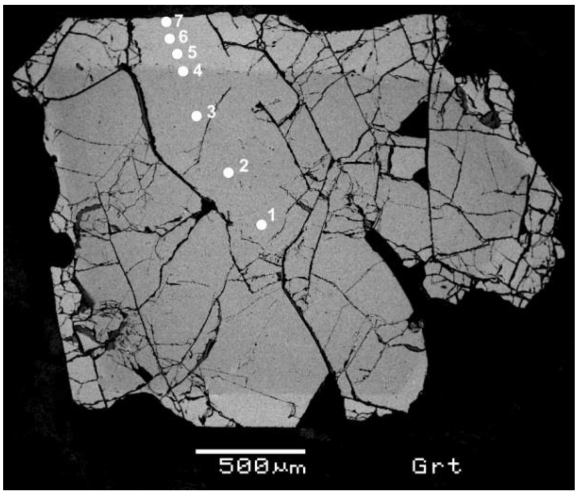

Figure 3. Backscattered electron (BSE) image of garnet crystal. Figures indicate disposition of analyzed points.

According to microprobe analysis and mineral composition data, the studied garnets are zonal (Fig. 3): the centre of the crystal is homogeneous, while the peripheral part is clearly zonal. The amount of FeO decreases slightly from the centre of the crystal to the periphery, while the amount of calcium and magnesium significantly decreases; a well-expressed increase in manganese content is recorded (Fig. 4). As for the variations in the composition of minerals, they also show the same picture: the variation in the content of almandine is insignificant, the amount of pyrope and grossular drops sharply from the centre to the periphery, while the number of spessartine increases (Fig. 5, Table 1).

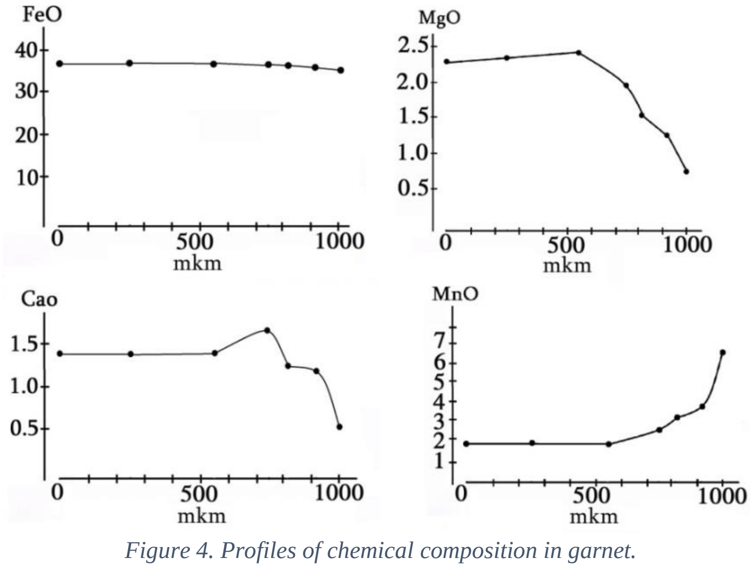

Figure 4. Profiles of chemical composition in garnet.

Previous researchers believed that garnet in biotite-garnet bearing granites is of assimilative origin, which was due to the assimilation of clay rocks by the granitic magma [12]. Our data do not prove this. The amount of Al_2O_3 in biotite-garnet-, biotite-hornblende-allanite- and biotite-microcline bearing granites is similar; biotite-garnet bearing granites do not have a high TiO_2 content typical of hybrid granites [10, 2]; Also, the increased amount of CaO characteristic of contaminated granites is not recorded, while its content is 0.7-45% in uncontaminated granites. The magnesium content and the spessartine molecule are reduced to 5%.

In our opinion, garnet formation took place in two stages: during the crystallization process of granitic magma and its subsequent post-magmatic stage. The core of the garnet was formed at the magmatic stage, in paragenesis Bt+Pl+Or+Grt+Qz (Mineral symbols are given as per Whitney and Evans [15]), but its periphery - at the cooling stage of granitic magma (probably at 450-500℃

temperature conditions), in paragenesis - Ab+Mc+Grt+Qz±Ms. This is based on the fact that existed in the rock the primary high-temperature plagioclases and potassium feldspars crystallized from the magma are transformed into low-temperature minerals (albite, which contains 1% anorthite molecule, and microcline, which contains 3% albite molecule) in the post-magmatic stage [3].

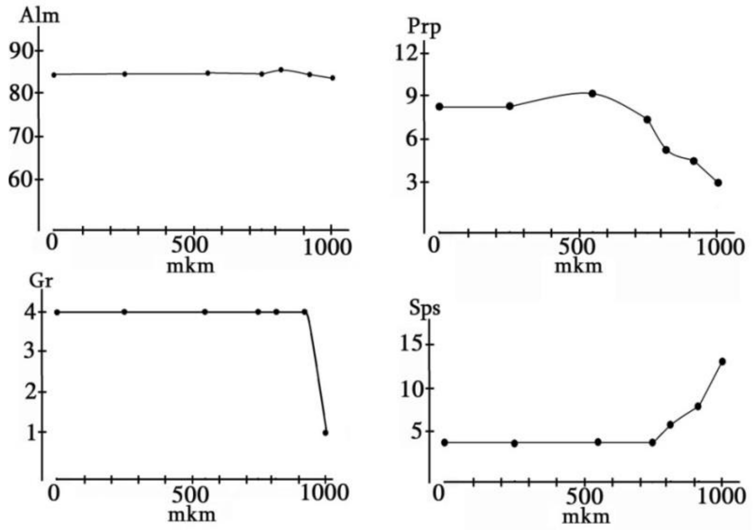

Figure 5. Profiles of minal content in garnet.

Although allanite is generally an accessory mineral, it is a rock-forming mineral in biotite-hornblende-allanite bearing granites of the Khrami crystalline massif [13, 14]. Allanite is presented as tabular and well-defined prismatic crystals of greenish-brown colour; Sometimes, it is twinned. Biotite and sometimes garnet occur as inclusions in allanite (Fig. 6). As for the presence of allanite in the other varieties of the granites distributed in the massif, it is appeared there as an accessory mineral and is spread sporadically.

Table 1. Microprobe analysis (wt.%) of garnet from biotite-garnet bearing granites of the Khrami crystalline massif (mean values of 9 crystals analysis)

Component	**Garnet analysis**						
	1 (Core)	2	3	4	5	6	7 (Margin)
SiO_2	36.39	36.47	36.43	36.48	36.18	36.59	36.81
Al_2O_3	20,91	20.86	20.76	20.77	20.84	20.60	20.48
FeO	37.01	36.90	36.81	36.86	36.87	36.59	35.70
MnO	1.87	1.94	1.9	2.31	3.06	3.79	6.49
MgO	2.27	2.29	2.37	1.96	1.53	1.23	0.70
CaO	1.43	1.43	1.44	1.55	1.25	1.18	0.53
Total	99.88	99.89	99.71	99.93	99.73	99.98	100.71
Si	2.96	2.96	2.96	2.97	2.96	3.00	3.01
Al	2.00	2.00	1.99	1.99	2.01	1.99	1.97
Fe^{3+}	0.08	0.07	0.08	0.07	0.07	0.02	0.01
Fe^{2+}	2.43	2.43	2.42	2.44	2.45	2.48	2.43
Mn	0.13	0.13	0.13	0.16	0.21	0.26	0.45
Mg	0.27	0.28	0.29	0.24	0.19	0.15	0.09
Ca	0.12	0.12	0.13	0.14	0.11	0.10	0.05
X_{Fe2+}	0.90	0.90	0.89	0.91	0.93	0.94	0.96
Alm	0.84	0.84	0.84	0.84	0.85	0.84	0.83
Prp	0.08	0.08	0.09	0.07	0.05	0.04	0.03
Sps	0.04	0.04	0.04	0.04	0.06	0.08	0.13
Grs	0.04	0.04	0.04	0.04	0.04	0.04	0.01

A microprobe study of allanite has also been carried out (Table 2). Determinations were carried out both in the core of the crystals and on its peripheries (Fig. 7). As a result of research, allanites of magmatic and post-magmatic genesis have been established [1]. Allanite of magmatic generation is characterized by well-defined crystalline forms and zoning and is often accompanied by secondary epidote rims (Fig. 6). Within the massif, allanite of metasomatic origin is also observed is characterized by irregular paddle-shaped crystals and various mineral inclusions. According to V.Lyakhovich [10], the concentration of large amounts of allanite in biotite-hornblende-bearing granites is related to calcium enrichment. He assumed that the increased amount of allanite in granites is related to the process of their assimilation with sedimentary rocks. According to our data, this view is not confirmed. It is paragenetic with apatite, zircon, sphene and magnetite, which appear during the crystallization stage of granitic magma.

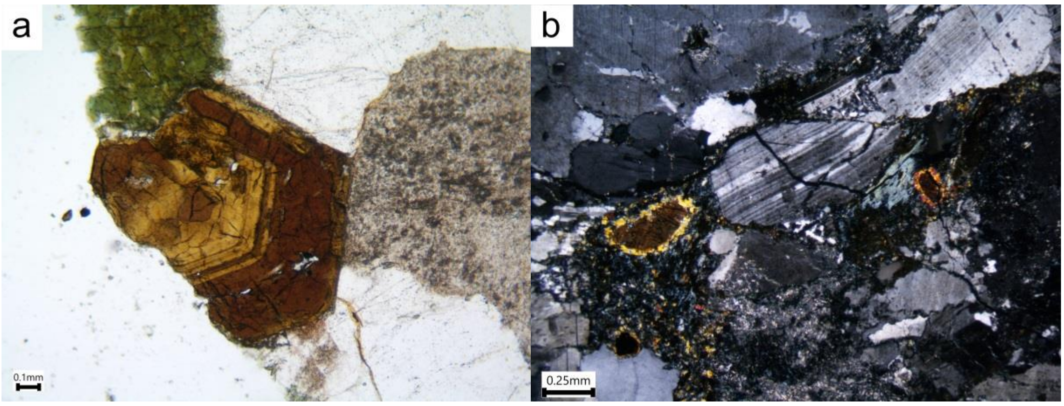

Figure 6. a) Zonal allanite, PPL and b) Allanite crystals with epidote rims, XPL.

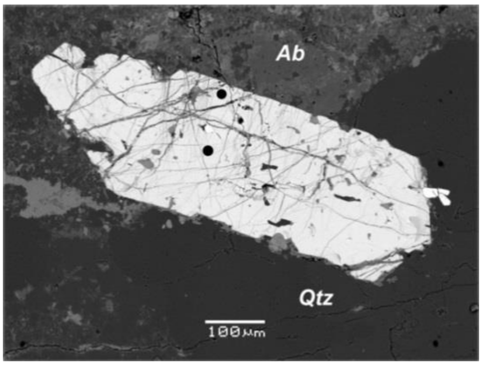

Figure 7. BSE image of allanite crystal from the Khrami crystalline massif rocks. Dots indicate disposition of analysis in the core and periphery of the crystal.

As a result of the research, it was established that the allanites of the Khrami massif granitoids belong to the cerium variety with a high content of Ce_2O_3, La_2O_3 and Nd_2O_3 [1]. The origin of allanite in biotite-microcline-, especially biotite-hornblende bearing granites, is due to the high concentration of REE in the granite magma and the introduction of calcium by hydrothermal solutions (Table 2).

Table 2. Microprobe analysis (wt.%) of allanites from the biotite-hornblende-allanite bearing granitoids of the Khrami crystalline massif (mean values of 6 grains analyses)

Wt, %	The Khrami massif (mean)	
	Periphery	Core
SiO_2	29.56	29.93
TiO_2	1.82	1.62
Al_2O_3	14.17	14.31
$FeO^{*\,total}$	16.77	16.32
MnO	0.20	0.23
MgO	0.34	0.29
CaO	10.20	10.02
SrO	-	0.14

ThO_2	0.84	0.68
La_2O_3	6.62	6.60
Ce_2O_3	12.00	12.12
Pr_2O_3	-	-
Nd_2O_3	3.92	3.36
Sm_2O_3	1.86	1.68
Gd_2O_3	0.11	0.09
Y_2O_3	0.16	0.13
Dy_2O_3	-	-
Er_2O_3	-	-
Yb_2O_3	-	-
UO_2	0.08	0.09
F	0.27	0.03
H_2O	1.60	1.93
Total	100.52	99.57

Conclusion

- The garnets from the biotite-granite bearing granites of the Khrami crystalline massif are zonal. In particular, the centre of the crystals is homogeneous, while the peripheral part is clearly zonal.
- Garnets of the massif were formed in two stages: during the crystallization process of granite magma and in its next - post-magmatic stage. The core of the garnet was formed in the magmatic stage, in paragenesis Bt+Pl+Or+Grt+Qz, but its periphery - in the cooling stage of granite magma, in paragenesis - Ab+Mc+Grt+Qz±Ms.
- The genesis of allanite in the biotite-hornblende-allanite bearing granites of the massif is due to the concentration of REE in the granite magma and the introduction of calcium by hydrothermal solutions.
- Allanites of biotite-hornblende-allanite bearing granites from the Khrami crystalline massif belong to the cerium variety with high Ce_2O_3, La_2O_3 and Nd_2O_3.

Competing interests

The authors declare that they have no competing interests.

Authors' contribution

All authors provided critical feedback and helped shape the research, analysis and manuscript.

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