PETROLOGICAL STUDY OF METASOMATIC ALTERED GRANITOIDS FROM KANARATA DEPOSIT, SAKAR MOUNTAIN, SOUTHEASTERN BULGARIA

Stefka Pristavova[1], Nikoleta Tzankova[1], Nikolay Gospodinov, Petyo Filipov[2]

[1] *University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; stprist@mgu.bg*
[2] *Geological Institute, Bulgarian Academy of Sciences, 1113, Sofia; p_philipov@geology.bas.bg*

ABSTRACT. The present article is a result of the study of the altered granitoid rocks cropping out in the north-eastern periphery of the Sakar batholith. The investigated rocks are enriched by amphibolite xenoliths and additionally, they are intensively metasomatically altered. The mineral composition of the studied rocks is presented by minerals of the amphibole group (Ca-Mg hornblende and barroisite), plagioclase (albite), quartz, K-feldspar (single grains), titanite, rutile, apatite, and zircon. The typical magmatic textures in the rocks are missing. The albite druses developed in the caverns represent intensively metasomatically re-worked amphibolite xenoliths, rutile, titanite, barroisite and apatite mineralisations that are genetically related to the process of Na-alteration. The dated U-Pb zircon population in the metasomatically altered granitoids shows igneous origin and the obtained data confirm the early Paleozoic age of the Sakar batholith.

Keywords: Sakar batholith, altered granitoid rocks, Na-metasomatites, albite druses

ПЕТРОЛОЖКО ИЗСЛЕДВАНЕ НА МЕТАСОМАТИЧНО ПРОМЕНЕНИ ГРАНИТОИДИ ОТ НАХОДИЩЕ КАНАРАТА, САКАР, ЮГОИЗТОЧНА БЪЛГАРИЯ
Стефка Приставова[1], Николета Цанкова[1], Николай Господинов, Петьо Филипов[2]
[1] *Минно-геоложки университет "Св. Иван Рилски", 1700 София*
[2] *Геологически институт, Българска академия на науките, 1113 София*

РЕЗЮМЕ. В тази статия са представени резултатите от изследването на променени гранитоиди, разкриващи се в североизточната периферия на Сакарския батолит. Изследваните скали са набогатени на амфиболитови ксенолити и допълнително са метасоматично променени с формиране на Na-метасоматити. Минералният състав на изследваните скали е представен от минерали от амфиболовата група (Ca-Mg амфибол и бароисит), плагиоклаз (албит), кварц, К-фелдшпат (единични зърна), титанит, рутил, апатит и циркон. Изследваните албитови друзи в кавернте, съдържащи титанит, рутил, бароазит, апатит, представляват метасоматично променени амфиболитови ксенолити. Датираните циркони са с магматичен генезис и получените данни потвърждават раннопалеозойската възраст на Сакарския батолит.

Ключови думи: Сакарски батолит, променени гранитоиди, Na-метасоматити, албитови друзи

Introduction

The Sakar granite batholith is well investigated during the years and a lot of information related to the mineralogy, petrology, structure features and geochemical specialisation has been published (Kamenov et al., 2010 and references therein). The accumulated data give us a relatively clear picture about the rocks in the batholith. The granites are emplaced into high-grade metamorphic frame represented by gneisses, gneiss-schists, amphibolites, meta-ultrabasites. These metamorphites are referred to the Prerhodopian Supergroup, Botourche Group – Zhalti Chal and Punovo Formations (according to Kozhoukharov et al., 1994) or to the late Paleozoic to early Mesozoic volcanic-sedimentary complex metamorphosed during Late Alpine together with the emplacement of the batholith (Ivanov et al., 2001; Gerdjikov, 2005). The following granite units are distinguished in the batholith: equigranular in the inner parts, porphyroid with large microcline megacrysts in the outer parts, and aplitoid-pegmatoides (Aleksandrovo type) in the north-eastern periphery. The presence of xenoliths from the hosted gneisses and amphibolites in the marginal parts of the batholith is a very

common characteristic. The distinguished modal petrographic species are quartz-monzodiorite, quartz-monzonite, granodiorite and granite (Kamenov et al., 2010).

According to the geological setting the age of Sakar batholith is determined as early Palaeozoic – the pieces of granites are included in the Permian (?) and Early Triassic conglomerates (Savov, 1988; Chatalov, 1990) or Late Jurassic–Early Cretaceous (Ivanov et al., 2001). The ages of 320±18 Ma (Zagorchev et al., 1989), 499±70 Ma (Lilov, 1990), and 250±35 Ma (Skenderov et al., 1986) are published according to Rb/Sr radioisotope ratio. Dated zircons (U-Pb) show the early Palaeozoic age of magmatic crystallisation – 300 Ma (Peycheva et al., 2016) and 295–296 Ma (Bonev et al., 2017).

The present study is focused on the rock outcrops from the north and north-eastern periphery of the Sakar batholith in the Kanarata deposit, north of the village of Hlyabovo (Fig. 1). These granites are enriched by the amphibolite xenoliths from the hosted metamorphic frame and they are affected by an intensive process of Na-metasomatic alteration – albitization. The process of irregular albitization was mentioned in the previous studies as a local, not dated process (for example

south of the village of Orlov Dol) and it was supposed that its time is later than the crystallisation of the batholith, maybe post-Triassic (Kamenov et al., 2010).

The relevance of this study is due to insufficient published data about the mineralogy and geochemistry of these metasomatic altered granites and some minerals into them

which represent valuable gemological samples. On the other hand, this natural raw material which is characterised by uniqueness, exhaustiveness and non-recoverability is extracted for feldspar material during the years which necessitate its timely study.
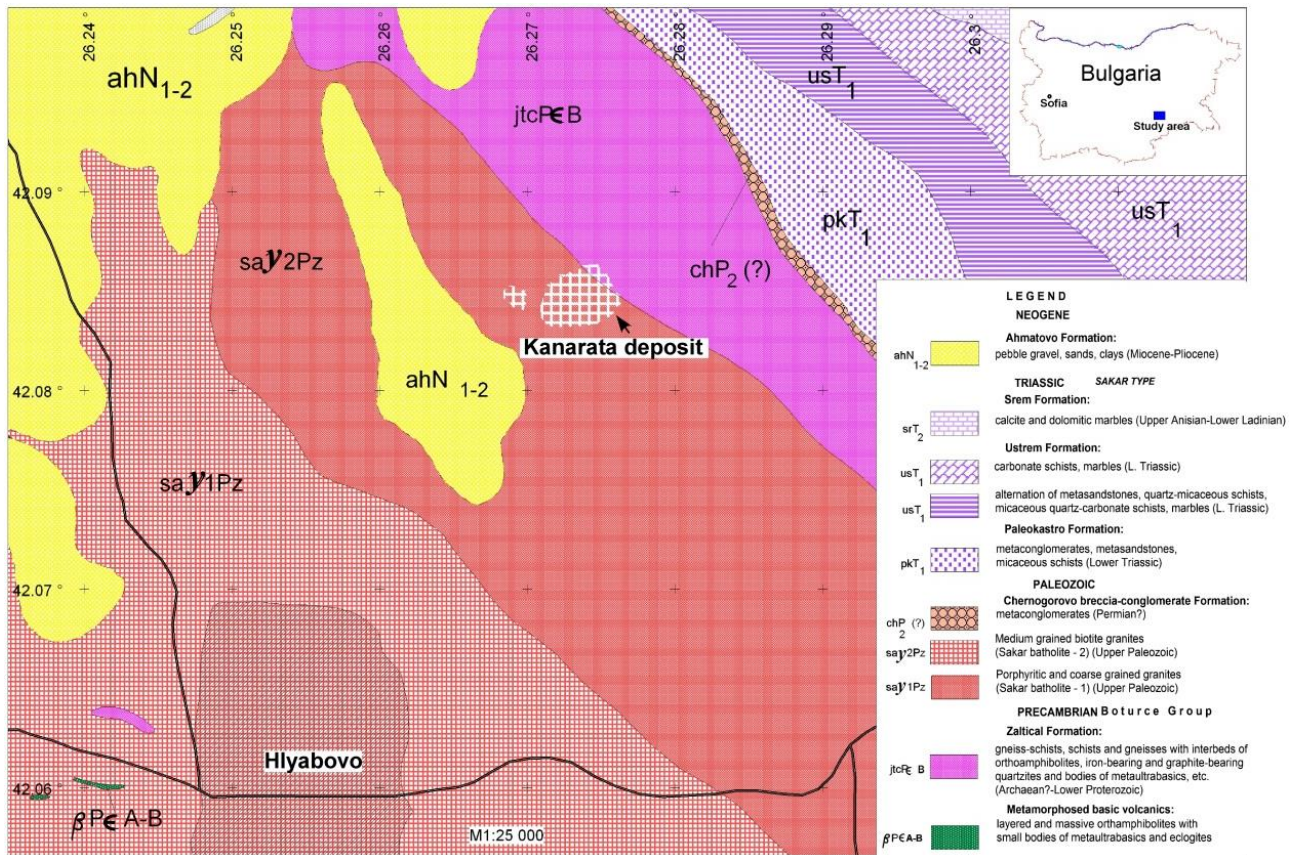

Fig. 1. Geological map of the studied area (after Kozhoukharov at al., 1994, with additional data)

Geological setting

The studied rocks are referred to the so-called Aleksandrovo type aplitod-pegmatoid granites. They outcrop close to the contact of the Sakar batholith with the metamorphic frame as elongated bodies and veins with east-western direction (Fig. 1). Minerals such as titanite, rutile, fibrous type amphibole, tourmaline, albite, epidote, molybdenite and etc. are established in these veins (Kozhoukharov et al., 1994).

In the frame of the Kanarata deposit intensively altered granitoids are revealed – leuco- to mesocratic medium grained with massive structure, fragile, strongly weathering. These rocks are enriched by lenses amphibolite xenoliths with sizes from 0.6 to 2.0 m. The boundaries with the hosted granites are intensively erased (Fig. 2a). Most of xenoliths are eroded and they are observed as caverns filled up by albite druses and minerals as rutile, titanite, apatite, minerals of amphibole group, chlorite, talc. (Fig. 2b).

Well-visible linear zones with variable thickness (from 5–20 cm up to 50–120 cm) are presented in the deposit. Along these zones, the rocks are altered and re-worked into whitish fine-to medium-grained varieties. The contacts are sharp ones with a

segregated accumulation of whitish component along them (Fig. 2c).

The dykes and quartz veins are observed among granitoids, also. The dykes are with thickness of up to 45–50 cm, light to dark grey in colour, fine porphyry with massive structure. Along dyke's contacts chlorite-talc (?) aggregates are formed (Fig. 2d). Grey to whitish quartz veins (thickness up to 20–35 cm) are observed in the frame of the deposit and some of them contain big crystals of rutile and molybdenite (Fig. 2e).

Materials and methods

The study material was selected from several places in the Kanarata deposit – granitoids, assimilated amphibolite xenoliths into them, zones with albitization and dykes.

The samples were optically studied using Stereo-microscope OLYMPUS and Leitz polarised microscope with Camera OLYMPUS S52 (for thin sections).

The chemical composition of the mineral was determined by Scanning Electron Microscopy fitted with Energy Dispersive Spectrometer (SEM-EDS) and Electron Microprobe Analyses.
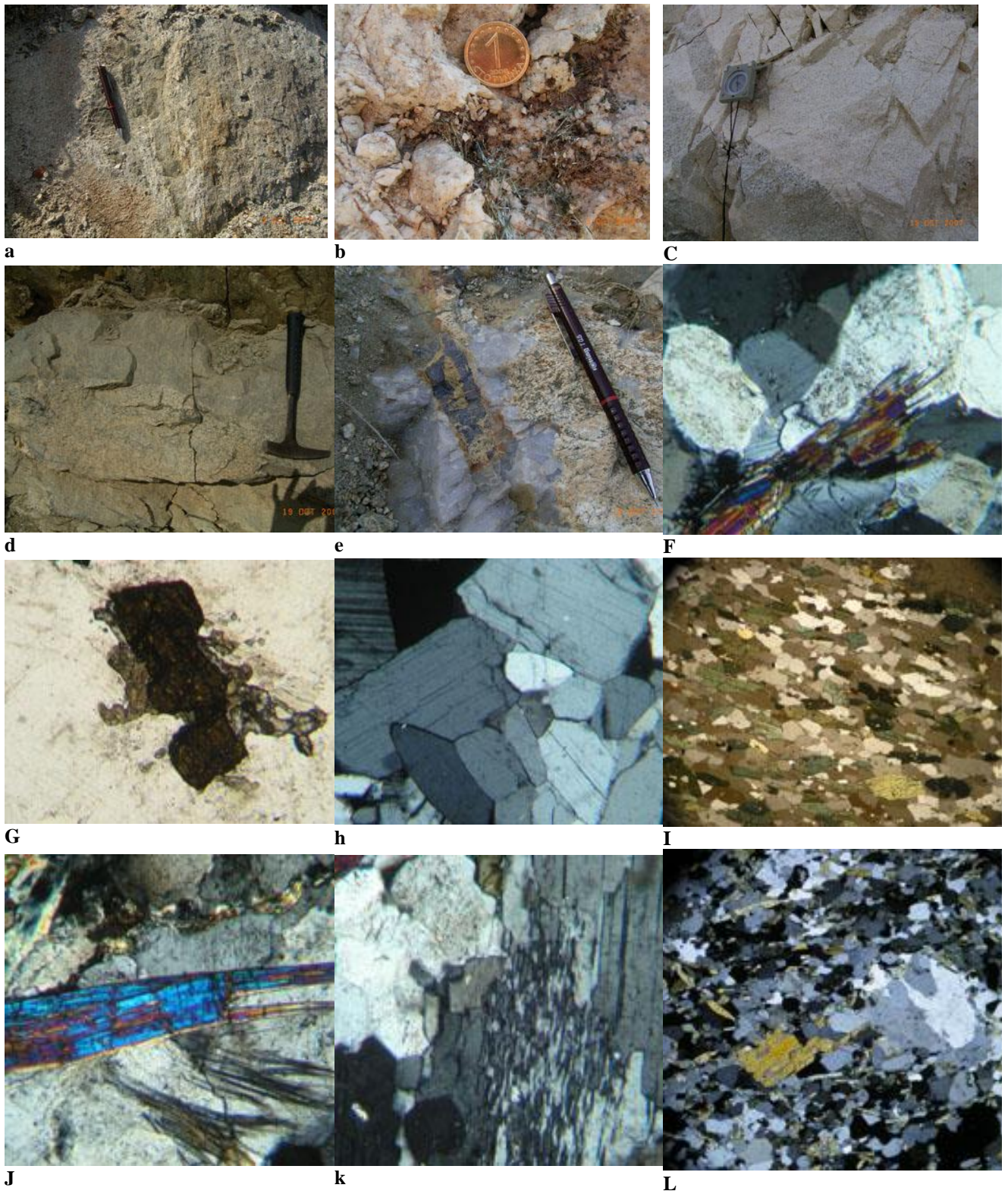
Fig. 2. Macro- and microphotos of studied rocks: *a*, amphibolite xenolith among granitoids; *b*, cavern filled up with albite and needles of amphibole mineral; *c*, linear zone of albitization; *d*, dyke among granitoids; *e*, quartz vein with molybdenite; *f*, amphibole crystal among plagioclase. CPL, Ob. F. W. = 1225 µm; *g*, rutile with "corona-like" of titanite, PPL, Ob. F. W. = 1225 µm; *h*, albite zone. CPL, Ob. F. W. = 1225 µm; *i*, general view of preserved amphibolite xenolith. CPL, Ob. F. W. = 1900 µm; *j*, barroisite crystals among albite. CPL, Ob. F. W. = 1225 µm; *k*, albite with with chest-board structure. CPL, Ob. F. W. = 1225 µm; *l*, general view of dike with porphyry crystals of amphibole and plagioclase. CPL, Ob. F. W. = 3900 µm

The analyses were performed on the representative samples using a JEOL at Eurotest-Control OOD. The chemical composition of the rocks was determined using AES ICP in the Laboratory of Geochemistry at the University of Mining and Geology "St. Ivan Rilski" and ICP-MS at the "AcmeLabs", Canada for the REE and trace elements.

A single sample of the albitized zone has been dated using U-Pb zircon geochronology. A total of 16 analyses were obtained on either autocrystic or antecrystic zircons and performed on New Wave UP193FX LA coupled to Perkin Elmer ELAN DRC-e quadrupole ICP-MS at the Geological Institute of the Bulgarian Academy of Sciences.

Results

Mineral and petrographic characteristics

The studied "granitoids" from the Kanarata deposit are represented by irregularly to regularly grained rocks with mineral composition of plagioclase, minerals of the amphibole group, quartz, sporadic grains of K-feldspar, titanite, rutile,

apatite, zircon and imposed secondaries of sericite, epidote group minerals, chlorite.

Amphibole (up to 15–20%) – irregularly represented as long prismatic crystals with sizes of 1.8 mm along the long axis or small (up to 0.2–0.4 mm) grains segregated into aggregates. The crystals are light greenish with traces of re-crystallisation with the formation of long prismatic crystals along periphery contours (Fig. 2f). The chemical composition, according to Leake et al. (1997), is determined as Ca-Mg hornblende (Table 1).

Plagioclase (up to 70–75%) – short prismatic crystals in sizes from 0.5 to 2.0 mm. It is presented by two generations, at least: 1) crystals with zonal structure (turbid central part with fine flaked sericite and epidote aggregates and clear periphery); 2) clear crystals some of them with chess-board structure. The An-content in plagioclase vary from 2.6 to 0.79 (Table 2).

Quartz (up to 5%) is irregularly presented in shape grains in limited quantity.

Table 1. *Chemical composition of amphiboles*

	1	2	3	4	5	6	7	8
SiO_2	54.74	55.77	56.48	51.38	56.81	55.03	55.41	47.95
TiO_2	0.06	0.08	0.00	0.12	0.00	0.08	0.08	0.21
Al_2O_3	3.42	3.06	2.78	4.89	1.56	3.85	3.77	9.03
FeO	3.66	3.59	3.69	7.00	6.18	4.13	4.02	10.09
MnO	0.21	0.12	0.00	0.07	0.00	0.00	0.22	0.27
MgO	23.99	24.49	24.30	22.05	23.70	24.46	24.85	18.56
CaO	11.00	10.75	11.12	9.81	10.80	9.98	10.39	10.98
Na_2O	0.86	0.00	0.00	2.15	0.00	1.16	0.00	1.46
K_2O	0.00	0.00	0.00	0.00	0.04	0.04	0.00	0.22
Σ	97.94	97.86	98.37	97.47	99.09	98.73	98.74	98.77
Numbers of ions on the basis of 23 O								
Si	7.275	7.320	7.411	6.956	7.449	7.187	7.167	6.556
Al^{4+}	0.536	0.473	0.430	0.780	0.241	0.593	0.575	1.444
Al^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.011
Fe^{3+}	0.407	0.394	0.405	0.792	0.678	0.451	0.435	1.154
Ti	0.006	0.008	0.000	0.012	0.000	0.008	0.008	0.022
Fe^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.024	0.013	0.000	0.008	0.000	0.000	0.024	0.031
Mg	4.753	4.792	4.754	4.451	4.633	4.762	4.792	3.783
Ca	1.566	1.512	1.563	1.423	1.517	1.396	1.440	1.608
Na	0.222	0.000	0.000	0.564	0.000	0.294	0.000	0.387
K	0.000	0.000	0.000	0.000	0.007	0.007	0.000	0.038
Σ	14.788	14.512	14.563	14.987	14.524	14.697	14.440	15.034
	Ca-Mg hornblende	Ca-Mg hornblende	Ca-Mg hornblende	Barroisite Na-Ca amph	Ca-Mg hornblende	Barroisite Na-Ca amph	Barroisite Na-Ca amph	Ca-Mg hornblende

1–3, altered granitoids; *4, 5*, amphibolite xenoliths; *6, 7*, albite druses; *8*, dyke

Table 2. *Chemical composition of plagioclases*

	1	2	3	4	5	6	7
SiO_2	66.89	66.11	66.55	66.9	66.31	63.28	62.48
Al_2O_3	19.44	19.85	20.11	19.86	20.39	22.22	23.25
FeO	0.00	0.00	0.00	0.00	0.11	0.06	0.09
CaO	0.19	0.50	0.62	0.12	0.05	3.05	3.26
Na_2O	13.12	12.85	12.90	12.98	11.73	9.73	9.90
K2O	0.00	0.00	0.00	0.00	0.00	0.09	0.04
∑	99.64	99.31	100.18	99.86	98.590	98.43	99.02
Numbers of ions on the basis of 32/O/							
Si	11.822	11.733	11.713	11.787	11.777	11.335	11.154
Al	4.049	4.152	4.171	4.124	4.268	4.691	4.892
Fe^{2+}	0.000	0.000	0.000	0.000	0.016	0.009	0.013
Ca	0.036	0.095	0.117	0.023	0.010	0.585	0.623
Na	4.495	4.421	4.402	4.434	4.039	3.379	3.426
K	0.000	0.000	0.000	0.000	0.000	0.021	0.009
∑	20.402	20.402	20.403	20.368	20.109	20.019	20.118
Mol. per cent of An, Ab and Or							
An	0.79	2.10	2.59	0.51	0.23	14.69	15.36
Ab	99.21	97.90	97.41	99.49	99.77	84.80	84.41
Or	0.00	0.00	0.00	0.00	0.00	0.52	0.22

1, 2, altered granitoids; *3,* amphibolite xenoliths; *4, 5,* albite druses; *6, 7,* dyke

Rutile – well rounded in shape crystals with sizes up to 0.1–0.2 mm grouped into aggregates. Around crystals, a thin "corona-like" structure of titanite is formed (Fig. 2g). The well-formed individual crystals of titanite are also presented. The rocks are enriched by the accessories apatite and zircon.

This mineral composition of the studied rocks is a result of the process of transformation of amphibolite xenoliths into "amphibole gneisses" during their granitisation and the imposed process of albitization. The typical magmatic textures are preserved only in limited places. The linear zones with processes of albitization have the same mineral composition where plagioclase (albite) build up more than 80% of the rock's volume forming hetero-hypidiomorphic texture (Fig. 2h).

The preserved amphibolite xenoliths are rarely observed. They are presented as fine crystalline rocks with well-expressed metamorphic foliation a clear boundary with the hosted granitoids (Fig. 2i) and mineral composition of minerals of amphibole group, plagioclase, quartz, sporadic grains of K-feldspar, titanite, rutile, apatite, zircon and imposed secondaries of sericite, epidote group minerals, chlorite and talc-serpentine(?) minerals. More frequently the xenoliths are totally affected by granitisation and imposed albitization and they are observed as caverns filled up by albite, amphibole group minerals, titanite, chlorite, and apatite. The amphibole mineral, here, is presented by dark greenish prismatic crystals (0.2–0.6 mm) with strong sub-parallel orientation and is regularly disseminated in the rock. It is presented by Ca-Mg hornblende and barroisite (Table 1). The last one is observed into albite caverns where it forms needle crystals with length of up to 10 mm (Fig. 2j) and chemical zoning expressed with decrease of Mg and increase of Na content from the centre to the periphery.

Plagioclase (up to 60%) is observed as isometric in shape albite grains with sizes of up to 0.2–0.4 mm. The grains are clear without of lamellar structure. In the caverns the plagioclase crystals are with sizes of up to 3.0 mm with chest-board structure (Fig. 2k) and An-member in the limit of 2.51–0.23 (Table 2). In the druses the albite crystals are up to 10.1–10.2 mm long with thickness of up to 6–7 mm. Their habit is represented by {001}, {010}, {110} and {201}. Some of the crystals are elongated parallel to the *a*-axis, with domination of {001} and {010}. The rest of the crystals are with platy shapes developed parallel to (010). There have been reports of crystal twins on albite law {010}. The albite crystals are white to colourless at the edges.

The caverns with albite are enriched by minerals as: apatite – long prismatic crystals (Dencheva, 2017), some intensively cracked or as clear fine needles; chlorite; rutile; titanite as clear and well-formed crystals.

Dykes are fine porphyry on plagioclase and amphibole rocks (Fig. 2l). The rock-forming minerals show weak sub-parallel orientation to the dyke's contacts. The amphibole is presented by Ca-Mg hornblende and the plagioclase by irregularly in shape spotted oligoclase crystals (Tables 1, 2). The specific feature of the dykes is the presence of rutile-titanite mineralisation reaching up to 5% of the rock's volume.

Petrochemical particularities

The published petrochemical data about the rocks of the Sakar batholith give us information about the calc-alkaline character and mixed plate margin orogenic and volcanic-arc with presence of mantle component in the magma source and crustal contamination (Kamenov et al., 2010; Bonev et al., 2017). The obtained chemical composition of the selected samples (Table 3) show the significant differences (see Kamenov et al., 2010) and they could be summarised in the following way: 1 – the studied rock samples are with lower contents of Fe_2O_3, CaO and K_2O and twice increased contents

of Na_2O and MgO; 2 – the lithophile elements as Rb, Ba, Cs and PEE are with lower contents; 3 – the contents of U and Th are higher (with the exception of sample 1). The processes of assimilation of amphibolite xenoliths and imposed Na-alteration (albitization) in the studied rocks are the main reasons for the mineral and chemical differences with the published data about granitoids from the Sakar batholith.

The significant differences of the chemical composition between rock affected by varying intensity of process of Na-alteration (whole rock and linear zone with intensive albitization) could also be found in the Kanarata deposit. For illustration of this process, the balance of components (after the oxide method of Barth) has been made of two samples (Table 4, 3–4). The variation of the main oxides is shown in Figure 3.

Table 3. *Chemical composition of the selected samples from studied rocks*

	1	2	3	4	5	6	7
SiO_2	62.85	65.38	65.39	67.28	57.24	68.17	56.19
TiO_2	0.64	0.9	0.85	0.08	1.97	1.09	1.05
Al_2O_3	18.43	17.23	18.56	19.81	15.01	15.33	16.86
Fe_2O_3	1.39	0.69	0.58	0.13	7.05	2.32	4.99
MnO	0.02	0.02	0.01	< 0.01	0.04	0.03	0.07
MgO	3.31	2.62	1.8	0.19	3.92	1.9	5.8
CaO	3.07	2.23	1.74	0.95	7.33	2.76	7.09
Na_2O	8.43	9.22	9.5	10.35	5.51	7.18	6.05
K_2O	0.39	0.33	0.29	0.31	0.37	0.34	0.38
Ba	31	8	14	8	13	22	26
Be	11	3	6	5	6	6	8
Cs	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rb	3.5	0.1	0.8	0.5	1.2	1.3	1.5
Sr	436.3	109.9	219.6	202.6	383.2	200.6	621.5
Co	3.6	1.9	2.1	0.5	6.4	5.7	12.5
Hf	5	7	5.7	3.2	10.4	7.7	5.1
Nb	14	17.6	37.3	15.8	12.8	16.4	14.2
Ta	1.3	1.8	3.5	3.8	0.9	1.9	0.7
V	62	76	46	12	280	118	198
W	<0.5	1.3	1.4	<0.5	0.5	3.7	<0.5
Zr	157.6	232.5	190.3	45.7	390.6	232.6	168
Y	17	20.5	14.4	3	65.9	18.6	28.3
La	150.5	21.5	23.1	5.5	27.9	17.8	30.4
Mo	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Cu	0.9	0.6	0.6	1	0.8	0.7	0.8
Pb	0.9	0.8	0.8	0.8	0.3	1.7	0.6
Zn	6	<1	3	<1	4	2	10
Ni	5.3	0.9	2.3	0.8	5.9	2.3	11.4
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Au	1.7	1.9	<0.5	1.5	<0.5	0.9	1.6
Hg	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ga	17.2	13.8	15.9	16.9	22.9	19.1	22.2
Sn	3	4	3	<1	5	5	3
As	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	<0.5
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	0.2
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	40.5	12.2	25.5	11.2	7.4	15.8	6.2
U	2.7	1.9	1.8	0.8	3.7	2	4.2
Ce	191	54.6	39.2	8.1	63.1	46.4	70.8
Pr	14.65	7.52	5.79	1.23	8.78	3.84	9.36
Nd	45.4	28.9	22.1	5.2	39.2	15.2	34
Sm	5.84	5.4	3.82	0.78	9.95	3.6	6.34
Eu	1.47	1.25	0.89	0.34	2.92	1.08	1.81
Gd	4.94	4.42	3.18	0.6	11.5	3.7	5.54
Tb	0.66	0.7	0.48	0.1	2	0.59	0.91
Dy	3.36	3.53	2.58	0.41	11.69	2.95	4.97
Ho	0.54	0.67	0.44	0.09	2.36	0.58	0.97
Er	1.71	1.91	1.41	0.31	6.97	1.7	2.9
Tm	0.24	0.27	0.2	0.05	0.99	0.26	0.4
Yb	1.62	1.95	1.41	0.32	6.34	1.88	2.8
Lu	0.24	0.3	0.22	0.07	0.93	0.3	0.44

1–3, altered granitoids; *4*, linear zone of albitization; *5, 6*, amphibolite xenoliths; *7*, dyke

Table 4. *Balance of components (a, absolute difference; b, as a percentage of the content in the whole rock)*

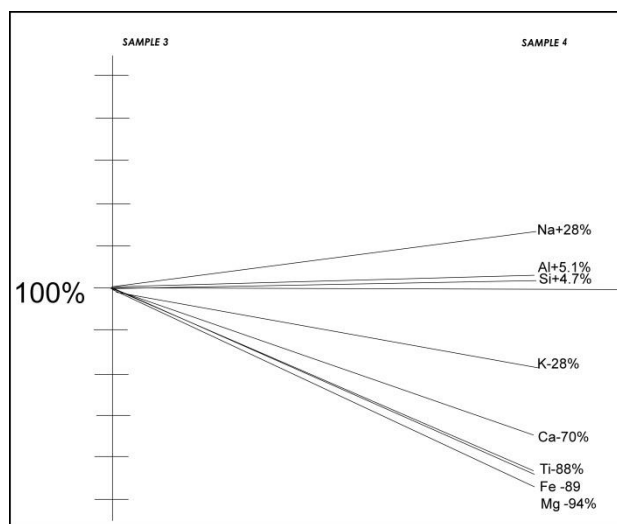| %	3	4	elements	A	b
SiO_2	62,85	67,28	Si	+ 2.65	+ 4.67%
TiO_2	0,64	0,08	Ti	- 0.38	- 88.00%
Al_2O_3	18,43	19,81	Al	+ 1.00	+ 5.10%
Fe_2O_3	1,39	0,13	Fe	- 0.86	- 89.00%
MnO	0,02	0,01	Mn		
MgO	3,31	0,19	Mg	- 4.17	- 94.00%
CaO	3,07	0,95	Ca	- 2.10	- 70.00%
Na_2O	8,43	10,35	Na	+2.97	+20.00%
K_2O	0,39	0,31	K	- 0.12	- 28.00%

Fig. 3. Changes of the contents of the main elements
Sample 3 – altered granitoid; Sample 4 – zone of albitization

U-Pb zircon dating of the albitized granitoid

Zircon crystals were separated from the whole-rock (intensively albitized zone in the granitoids) using heavy liquids, then hand-picked and fixed in epoxy resin before polishing. Cathodoluminescence (CL) and back-scattered (BSE) images have been taken in order to study the internal structure and zonation of crystals. Laser crater of 35 μm, ablation frequency of 8 Hz and detection time within 0.002–0.003 s were used for all measurements that were calibrated with GEMOC-GJ1 zircon (Jackson et al., 2004) as external standard for fractionation correction. Fractionation correction and results were estimated using GLITTER 4.0 software (Macquarie University). Diagram plots and Concordia ages are delivered with only the concordant analyses using Isoplot 4.15 (Ludwig, 2011) application.

Zircons from albitized granitoid are with short to long prismatic and rarely pyramidal shapes (Fig. 4a, b). Resorption structures are relatively frequent and are mostly visible near cores. Crystals cored by unzoned re-crystallised interiors and rimmed by oscillatory terminations are very common (Fig. 4a, b). The Th/U ratio, varying within 0.37–1.77, is indicative of the magmatic origin for all the zircons. Inherited zircons and xenocrysts have not been identified over the course of this study, but the antecrystic zircons comprise considerable portion of all crystals analysed.

Half of analyses are interpreted to belong to antecrysts (329.79–311.23 Ma) incorporated in rocks derived from older magmatic pulses (Fig. 4d). Autocrystic zircon populations are aged, the youngest within 303.12–296.60 Ma, forming Concordia age at 298.4±1.6 Ma (Fig. 4c) and considered to reflect the timing of emplacement of Sakar granite. The obtained data confirm the Early Paleozoic age of magmatic crystallisation (Peycheva et al., 2016; Bonev et al., 2017).

Table. 5. *LA-ICP-MS isotopic ratios ($^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$, $^{208}Pb/^{232}Th$) and $^{206}Pb/^{238}U$, and $^{207}Pb/^{235}U$ ages of zircons from the altered granitoids (● analysis of autocrystic zircon; ∗discordant value; ⁑ analysis of antecrystic zircon)*

| N	Zr	Comment	Isotope ratios $^{206}Pb/^{238}U$	2 SE	$^{207}Pb/^{235}U$	2 SE	$^{208}Pb/^{232}Th$	2 SE		$^{206}Pb/^{238}U$	2 SE	$^{207}Pb/^{235}U$	2 SE	Th/U
									Rho	Age, Ma		Ratio		
1	2r	●	0.0481	0.0007	0.3499	0.0189	0.0174	0.0017	0.61	303.12	8.61	304.61	28.12	0.47
2	5c	∗	0.0515	0.0006	0.3925	0.0133	0.0158	0.0015	0.64	324.00	7.60	336.19	19.23	0.44
3	5r	⁑	0.0486	0.0008	0.3362	0.0215	0.0158	0.0017	0.60	306.01	9.22	294.28	32.31	0.42
4	7	⁑	0.0525	0.0009	0.3833	0.0293	0.0162	0.0017	0.60	329.79	11.02	329.46	42.35	1.12
5	8	⁑	0.0501	0.0008	0.3639	0.0258	0.0159	0.0017	0.59	315.25	9.82	315.15	37.97	1.28
6	13c	∗	0.0455	0.0006	0.3671	0.0158	0.0093	0.0010	0.62	287.05	7.27	317.52	23.32	1.77
7	13r	●	0.0474	0.0006	0.3462	0.0159	0.0150	0.0012	0.61	298.51	7.75	301.89	23.75	0.49
8	12	⁑	0.0495	0.0007	0.3603	0.0160	0.0161	0.0013	0.61	311.23	7.98	312.40	23.67	0.50
9	25r	⁑	0.0509	0.0007	0.3749	0.0158	0.0161	0.0013	0.62	320.13	8.09	323.30	23.11	0.67
10	25c	●	0.0472	0.0008	0.3420	0.0259	0.0183	0.0018	0.59	297.53	10.09	298.67	38.66	0.37
11	28c	●	0.0474	0.0007	0.3452	0.0180	0.0130	0.0011	0.61	298.62	8.37	301.11	26.96	0.80
12	28r	⁑	0.0514	0.0007	0.3757	0.0194	0.0147	0.0013	0.61	322.96	8.83	323.90	28.36	0.49
13	35c	⁑	0.0501	0.0006	0.3619	0.0143	0.0151	0.0013	0.62	314.91	7.73	313.66	21.16	0.67
14	35r	●	0.0471	0.0006	0.3380	0.0156	0.0147	0.0014	0.61	296.60	7.75	295.67	23.43	0.53
15	41r	●	0.0471	0.0007	0.3379	0.0168	0.0142	0.0015	0.61	296.90	8.00	295.56	25.35	0.53
16	46	∗	0.0496	0.0007	0.3280	0.0173	0.0140	0.0015	0.61	312.27	8.47	288.04	26.18	0.57
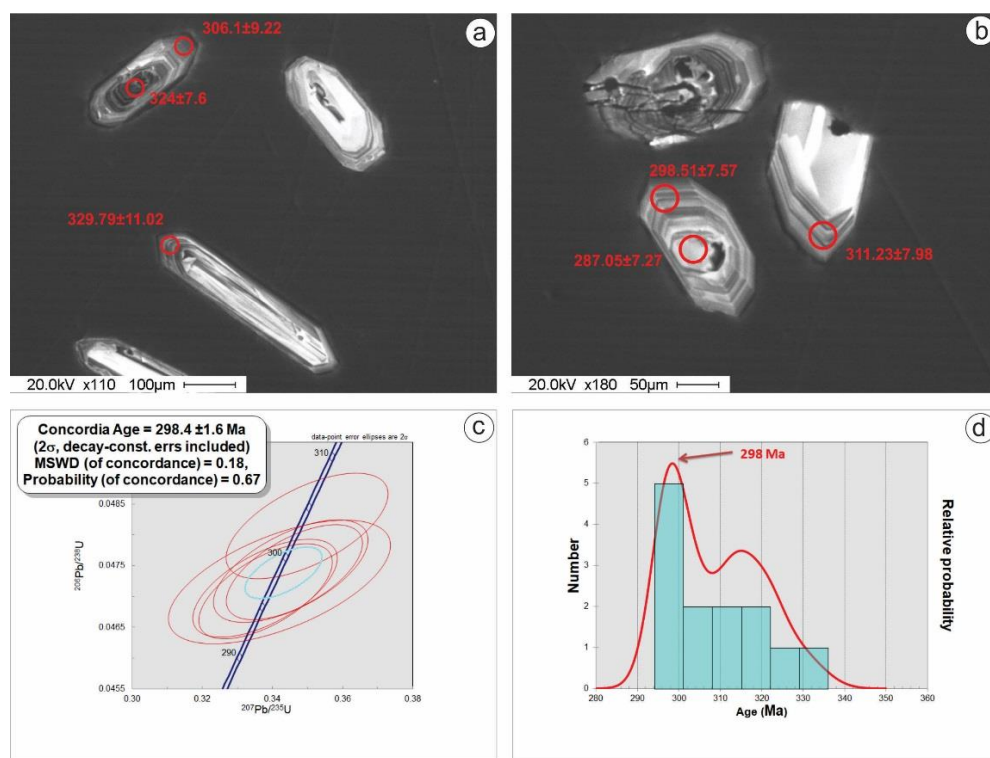
Fig. 4. Zircons from the studied albitized granitoids

Discussion and conclusion

The studied rocks from the Kanarata deposit are situated in the periphery area of the Sakar batholith. These rocks are characterised by completely different mineralogical and petrochemical characteristics as compared to the three distinguished granite units of the batholith. This is a result of the assimilation of the amphibolite xenoliths from the hosted high-grade metamorphic frame and superimposed intensive process of Na-alteration (albitization). The main characteristics of these rocks could be summarised as follows:

– The typical magmatic textures in the rocks are missing;

– The mineral composition is presented by minerals of the amphibole group (Ca-Mg hornblende and barroisite), plagioclase (albite), quartz, K-feldspar (single grains), titanite, rutile, apatite, zircon and imposed secondaries of sericite, epidote group minerals, chlorite;

– The superimposed process of albitization affects all rocks in the area of the deposit and it is most intensively developed along linear zones with east-west direction;

– The albite druses developed in the caverns represent intensively metasomatically re-worked amphibolite xenoliths and rutile, titanite, barroisite, and apatite mineralisations are genetically related to the process of Na-alteration;

– The increased content of MgO in the studied rocks and the presence of Mg-containing minerals could be a result of the assimilation of amphibolite xenoliths or a result of Mg-Na metasomatic process (?);

– The dated U-Pb zircon population in the metasomatically altered granitoids shows igneous origin and the obtained data confirm the Early-Paleozoic age of the Sakar batholith. The question about age of the process of albitization is still open.

The followed detailed study will clarify the mineralogy particularities of the Ti-containing minerals in the area and date the process of albitization.

References

Bonev, N., P. Filipov, R. Moritz, R. Raicheva, M. Borisova. 2017. Ordovician and Carboniferous-Permian magmatism in the Sakar unit of the Sakar-Strandzha zone, Bulgaria. – In: *National Scientific Conference "Geosciences 2017"*. Bulg. Geol. Soc., Sofia, 47–48.

Dencheva, S. 2017. Apatite from Sakar Mountain, Bulgaria – morphology and physical properties. – In: *National Scientific Conference "Geosciences 2017"*. Bulg. Geol. Soc., Sofia, 21–22.

Gerdjikov, I. 2005. Structure of the metamorphic basement in the northern part of Sakar unit, SE Bulgaria. – *C. R. Acad. Bulg. Sci.*, *58*, 3, 289–296.

Ivanov, Z., I. Gerdzhikov, A. Kunov. 2001. New data about structure and tectonic evolution of the Sakar region. – *Ann. Univ. de Sofia, Fac. gèol et gèogr., 91*, Liv. 1 – gèol., 35–80.

Jackson, S. E., N. J. Pearson, W. L. Griffin, E. A. Belousova. 2004. The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U–Pb zircon geochronology. – *Chemical Geology, 211*, 47–69.

Kamenov, B., V. Vergilov, H. Dabovski, I. Vergilov, L. Ivchinova. 2010. The Sakar batholith – petrology,

geochemistry and magmatic evolution. – *Geochem., Mineral. and Petrol., 48*, 1–37.

Kozhoukharov, D. 1988. Precambrian in the Rhodope massif. Lithostratigraphy. – In: Zoubek V. (Ed*.). Precambrian in Younger Fold Belts – European Variscides, the Carpathians and Balkans*. John Wiley & Sons, Chichester, 726–746.

Kozhoukharov, D., S. Savov, G. Chatalov, E. Kozhoukharova, I. Boyanov, E. Chelebiev. 1994. *Geological Map of Bulgaria on Scale 1:100000. Topolovgrad Map Sheet*. Committee of Geology and Mineral Resources, Geology & Geophysics, Sofia.

Leake, B., A. Wooly, C. Arps, W. Birch, M. Gilbert, J. Grice, F. Hawthorne, A. Kato, H. Kisch, V. Krivovichev, K. Linthout, J. Laird, J. Mandarina, W. Maresch, E. Nickel, N. Rock, J. Schumacher, D. Smith, N. Stephenson, L. Ungaretti, E. Whittaker, G. Youzhi. 1997. Nomenclature of amphiboles: report of the subcommittee on amphiboles of the international mineralogical association, commission on new minerals and mineral names. – *Canad. Mineral.*, *35*, 219–246.

Lilov, P. 1990. Rb-Sr and K-Ar dating of the Sakar granitoid pluton. – *Geologica Balc.*, *20*, 6, 53–60 (in Russian with English abstract).

Ludwig, K. R. 2011. *User's Manual for Isoplot/Ex, Version 4.15. A Geochronological Toolkit for Microsoft Excel.* – Berkeley Geochronology Center Special Publication 4, Berkeley, CA, USA.

Peytcheva, I., S. Georgiev, A. von Quadt. 2016. U/Pb ID-TIMS dating of zircons from Sakar-Strandzha Zone: new data and old questions about the Variscan orogeny in SE Europe. – In: *National Scientific Conference "Geosciences 2016"*. Bulg. Geol. Soc., Sofia, 71–72

Savov, S. 1988. Obzor stroenia Sakarskoi oblasti. – In: *Lineament kak Strukturi Sochlenenia Raznovuzrastnih Skladchatih Oblastei i Metalogenii.* Publ. House Bulgarian Academy of Sciences, Sofia, 98–114 (in Russian).

Savov, S., H. Dabovski. 1979. Metamorphic Triassic in the Topolovgrad syncline and its basement. – In: *Precambrian of the Rhodope Massive and the Embracing Phanerozoic Metamorphic Formation*. Publ. House Bulgarian Academy of Sciences, Sofia, 98–105 (in Russian with English abstract).

Skenderov, G., I. Palshin, Y. Mihailov, I. Bozhkov, L. Savova. 1986. About age of the Sakar granite pluton (South-East Srednogorie). – *Geochem., Mineral. and Petrol.*, *22*, 69–80 (in Russian with English abstract).

Zagorchev, I., P. Lilov, S. Murbat. 1989. Rb/Sr and K/Ar results of metamorphic and igneous rock from South Bulgaria. – *Geologica Balc.*, *19*, 3, 41–54 (in Russian with English abstract).