ГОДИШНИК НА МИННО-ГЕОЛОЖКИЯ УНИВЕРСИТЕТ "СВ. ИВАН РИЛСКИ", Том 48, Св. I, Геология и геофизика, 2005
ANNUAL OF THE UNIVERSITY OF MINING AND GEOLOGY "ST. IVAN RILSKI", Vol. 48, Part I, Geology and Geophysics, 2005

CHEMICAL CHARACTERIZATION OF GARNET AND P-T CONDITIONS OF METAMORPHISM OF THE TRIASSIC ROCKS OCCURRING TO THE SOUTH OF ORESHNIK, SOUTH-EAST BULGARIA

Nikoleta Tzankova

University of Mining and Geology „St. Ivan Rilski"; Sofia 1700

ABSTRACT. This study provides data about the chemical composition of garnet and associated minerals from the quartz-mica schists occurring to the south of the village Oreschnik, Sakar Mountain, and coustrains the P-T conditions of metamorphism. The chemical composition of the following minerals have been studied by electron microprobe: garnet, biotite, staurolite, white mica, chlorite, plagioclase. The metamorphic grade is of lower amphibolite facies. The P-T estimate for a staurolite - garnet - white mica - biotite - chlorite - plagioclase schist is T = 616^0 C, σ (T) = 21 and P = 7,8 kbar, σ (P) = 1.3.
Key words: garnet, amphibolite facies, metamorphism, Sakar Mountain

ХИМИЧНА ХАРАКТЕРИСТИКА НА ГРАНАТ И Р-Т УСЛОВИЯ НА МЕТАМОРФИЗМА НА ТРИАСКИТЕ СКАЛИ, РАЗКРИВАЩИ СЕ ЮЖНО ОТ ОРЕШНИК, ЮГОИЗТОЧНА БЪЛГАРИЯ

Николета Цанкова
Минно-геоложки университет "Св. Иван Рилски"; София 1700

РЕЗЮМЕ. Настоящата работа има за цел да предостави данни за химичния състав на граната и минералите от неговата асоциация в кварц – слюдени шисти, разкриващи се на юг от село Орешник, Сакар планина и за P–T условията на метаморфизма. Химичният състав на следните минерали беше изследван с помощта на електронно-микросондови анализи: гранат, биотит, ставролит, мусковит, хлорит, плагиоклаз. Регионалният метаморфизъм е от ниска степен на амфиболитовия фациес. Изчислените Р-Т условия за ставролит – гранат – мусковит – биотит – хлорит – плагиоклаз – съдържащите шисти са T = 616^{0}C, σ (T) = 21 и P = 7,8 kbar, σ (P) = 1.3.
Ключови думи: гранат, амфиболитов фациес, метаморфизъм, Сакар планина

Introduction

Mineral and chemical data for the garnet and staurolite bearing mineral parageneses in the quartz-mica schists occurring to the south of the village Oreshnik in the eastern slopes of the Sakar Mountain has been provided, as well as determination of the P-T conditions of metamorphism. These rocks are part of the Ustrem Formation, which has been introduced by Čatalov (1985) with the type area being in the Topolovgrad region. They are upper Lower Triassic in age. The metamorphic type of the Triassic in the studied region was first recognized in 1965 (Bojanov et all. 1965) from the southern slopes of the Sakar Mountain and later from the Maritza zone in 1968 (Kozhoukharov et all., 1968).

Geology

The lithostratigraphic dismemberment of the metamorphic Triassic integrates the rocks from the eastern slopes of the Sakar Mountain in the so called Topolovgrad Supergroup, which is subdivided into three formations – Paleokastro, Ustrem and Srem Formation. The Paleokastro Formation is built up of metaconglomerates, metasandstones and mica-schists. The Ustrem Formation is represented by: a) quartz-mica schists containing porphyroblasts of biotite, garnet and staurolite; b) garnet-amphibole, epidote-zoisite and quartz-amphobole schists; c) calc-schists; d) white, grey and striped marbles. The Srem Formation is built up of calcic and dolomitic marbles. The rocks of the Ustrem Formation are situated on the rocks of the Paleokastro Formation and are covered by the marbles of the Srem Formation. The Paleokastro Formation is related to the lower parts of the Lower Triassic, the Ustrem Formation includes the Upper part of the Lower Triassic and the Srem Formation belongs to the Middle Triassic. The Paleokastro Formation is of a continental (alluvial) origin. The other two formations are supposed to be of marine genesis (Čatalov, 1985; Kozhukharov, 1996).

Petrography

The studied garnets occur in quartz-mica schists to the south of the village Oreshnik in the direction towards the so called "Black Stones" region (Fig. 1). Macroscopically the rocks are fine-grained and of dark grey colour. They are granolepidoblastic and porphyroblastic containing biotite and garnet (up to 0.1-0.2 cm in size) and hughe staurolite 12 x 3 x 1,8 cm in size (Kostov et al., 1964). The garnets are raspberry-red coloured with week purple hue. They are euhedral and a common form appears to be {110}. Crystals with small additional {211} faces, which display rounded rhombododecahedral edges were also observed.

The staurolite crystals are dark brown coloured. They are prismatic in habit and show pseudohexagonal basal sections. Twins are common. The mineral assemblage additionaly includes white mica, chlorite, oligoclase and quartz. Chlorite is observed as tabular crystals and commonly shows twinning. Accessory minerals are tourmaline, ilmenite and as inclusions in biotite – calcite and a radioactive mineral forming pleochroitic haloes.

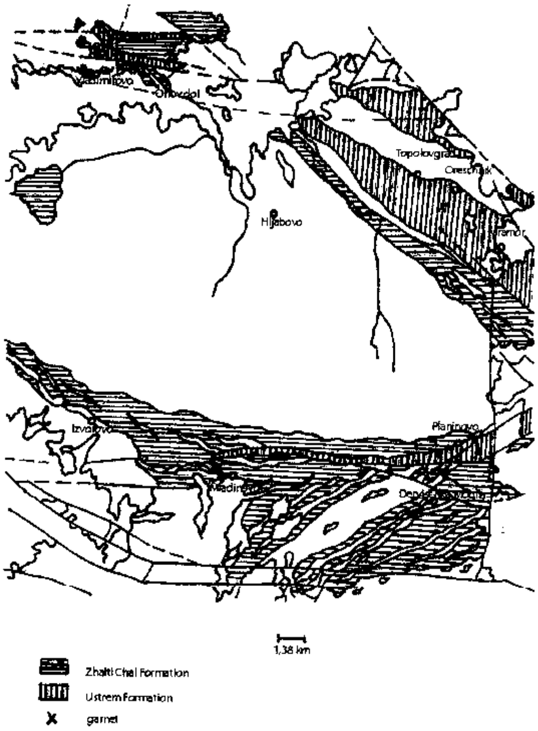

Fig. 1. Scheme of garnet outcropes in the metamorphic schists occuring to the south of village Oreshnik, South – East Bulgaria; x – garnet

In thin sections these garnets are pale rose-coloured, euhedral, fresh and mostly free of inclusions except of a few quartz inclusions. Biotite includes small flakes of white mica. Staurolite has abundant inclusions of quartz, garnet, biotite and ilmenite. Staurolite is not found as inclusion in garnet, but garnet is frequently observed as inclusion in staurolite.

Mineral composition

The chemical compositions of the minerals were studied by electron microprobe analyses (ARL-SEMQ S30, 4 spectrometers, EDS Link, 20 KV, 20 nA, standart kaersutite; University of Leoben, Austria). The garnets are almandine rich. They contain up to 77 -78 mol. % of the almandine endmember, up to 15 mol. % of pyrope endmember and minor other elements (Table 1, Fig. 2). All studied garnets show growth zoning. This is documented by an increase in FeO and MgO from core to rim and enrichment MnO and CaO in the cores. The explanation for the high Mn-content at the garnet cores is that garnet strongly fractionate Mn relative to other minerals, resulting in bell-shaped Mn profiles, which are caused by depletion of Mn in the rock through concentration of Mn in the first garnet nuclei to form. Successive layers of garnet overgrowing the core would then have a depleted reservoir of manganese to draw upon, and would therefore become progressively less manganiferous (Tracy, 1985).

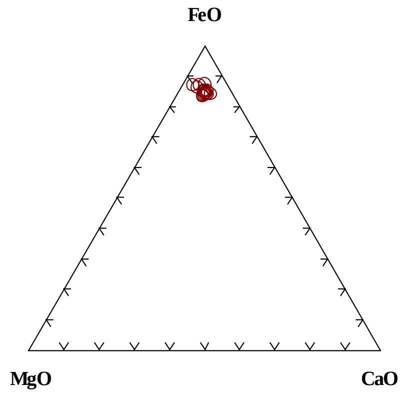

Fig. 2. The relative proportions of endmember molecules for garnets in the quartz-mica schists, Oreshnik

All studied garnets are one-phase and continuously zoned. That is there are no breaks or gaps in the zoning trends and there are no reversals (see Fig. 3). The garnet profile is made by spot analysis at intervals of 2 microns.

Chemical compositions of the minerals of the garnet-bearing paragenesis is shown in Table 2. The plagioclase is oligoclase with endmembers: Ab = 83,316%, An = 16,513% and Or = 0,205%. Electron microprobe analyses of rims and cores of biotite and staurolite show chemical zoning of these minerals with respect to iron. Biotite and garnet rims are enriched in FeO though X_{Mg} of garnet shows an increase towards the rims. An inverse correlation exists between the values of the same oxide at the rim and the core in the staurolite.

Thermobarometry

The P-T conditions of metamorphism for quartz-mica schists occurring to the south of the village Oreshnik, Sakar Mountain, are made using two different methods: conventional geothermobarometry using GTB Program Thermobarometry (*GTB*, 2001) and average pressure and temperature calculations based on an internally consistent thermodynamic data using Thermocalc 3.1 (*Thermocalc*, 2001). Activities were calculated with the program aX.2000 (*Mineral…*, 2000).

Table 1

*Chemical composition and endmembers of the garnets; * - garnet rim close to biotite*

	9-1 rim	9-1 core	9-1* rim	9-5 rim	9-5 core	9-5* rim	9-6 rim	9-6 core	9-6 rim	9-7 core	9-7 rim
SiO_2	36.970	36.910	37.380	36.640	36.940	36.560	36.410	37.650	37.820	37.680	40.240
TiO_2	0.060	0.070	0.070	0.040	0.070	0.000	0.040	0.070	0.030	0.040	0.000
Al_2O_3	21.070	19.080	19.280	19.350	20.120	19.690	20.340	22.380	19.930	20.050	19.410
Cr_2O_3	0.020	0.020	0.040	0.040	0.000	0.000	0.000	0.000	0.020	0.000	0.040
FeO	35.530	33.480	36.430	36.340	35.280	34.990	35.250	30.100	37.420	36.290	33.950
MnO	0.470	4.640	0.770	0.730	1.460	0.510	0.530	2.610	0.390	1.360	0.550
MgO	3.290	2.340	3.230	3.360	2.960	3.670	3.590	2.160	3.820	3.050	3.710
CaO	3.290	2.700	2.360	3.580	3.920	3.520	3.480	3.690	2.360	3.490	1.490
TOTAL	100.700	99.240	99.560	100.080	100.750	98.940	99.640	98.660	101.790	101.960	99.390
Formula											
Si	2.937	3.019	3.020	2.949	2.945	2.962	2.929	3.021	2.988	2.981	3.201
Al IV	0.063	0.000	0.000	0.051	0.055	0.038	0.071	0.000	0.012	0.019	0.000
Ti	0.004	0.004	0.004	0.002	0.004	0.000	0.002	0.004	0.020	0.002	0.000
Al VI	1.910	1.840	1.836	1.785	1.836	1.842	1.858	2.117	1.844	1.851	1.820
Cr	0.001	0.001	0.003	0.003	0.000	0.000	0.000	0.000	0.001	0.000	0.003
Fe^{3+}	0.166	0.114	0.144	0.262	0.234	0.201	0.211	0.000	0.166	0.164	0.000
Fe^{2+}	2.194	2.176	2.318	2.183	2.119	2.170	2.161	2.020	2.306	2.236	2.259
Mn	0.032	0.321	0.053	0.050	0.099	0.035	0.036	0.177	0.026	0.091	0.037
Mg	0.390	0.285	0.389	0.403	0.352	0.443	0.430	0.258	0.450	0.360	0.440
Ca	0.280	0.237	0.204	0.309	0.335	0.306	0.300	0.318	0.200	0.296	0.127
TOTAL	7.977	7.997	7.971	7.997	7.979	7.997	7.998	7.915	8.013	8.000	7.887
Endmembers											
Py	13.467	9.440	13.124	13.684	12.117	14.997	14.691	9.304	15.091	12.068	15.368
Alm	75.760	72.077	78.205	74.126	73.943	73.460	73.830	72.845	77.331	74.958	78.903
Spess	1.105	10.633	1.788	1.698	3.408	1.185	1.230	6.383	0.872	3.051	1.292
Gross	8.896	7.392	6.382	9.149	10.228	9.340	9.205	11.468	6.153	9.115	4.436
Andr	0.773	0.458	0.500	1.343	1.304	1.019	1.045	0.000	0.554	0.808	0.000

Table 2

Electron microprobe analyses of biotite, white mica, chlorite, staurolite, plagioclase and tourmaline; $X_{Fe}=Fe^{2+}/(Fe^{2+}+Mg)$, $X_{Mg}=Mg/(Fe^{2+}+Mg)$

	9-1bi c	9-1 bi rim	9-5bi core	9-5bi rim	9 bi2 core	9 bi2 rim	9-3 ms	9-5 ms	9 chl	9`chl core	9` chl rim	9 st core	9 st rim	9 pl	9 tourm
SiO_2	35.72	35.07	37.14	36.62	36.41	37.25	47.21	49.44	24.99	25.63	25.34	30.39	28.12	65.47	43.29
TiO_2	1.21	1.41	1.66	1.73	1.58	1.47	0.41	0.34	0.15	0.08	0.11	0.78	0,62	0.00	0.04
Al_2O_3	19.36	20.53	17.88	18.10	17.36	16.91	37.66	33.74	21.29	21.29	22.26	48.86	54,23	22.68	42.49
FeO	17.86	18.16	18.28	19.69	18.23	19.09	0.87	0.99	22.75	22.43	23.09	15.11	13,72	0.12	0.42
MnO	0.00	0.02	0.00	0.00	0.00	0.04	0.00	0.00	0.04	0.08	0.02	0.00	0	0.00	0.04
MgO	12.03	11.32	13.38	13.91	13.53	13.03	0.53	1.07	19.28	19.41	19.26	2.23	2,32	0.00	0.00
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.03	0.02	0,01	3.47	0.66
Na_2O	0.12	0.12	0.35	0.12	0.23	0.47	1.71	1.15	0.00	0.00	0.00	0.22	0	9.67	3.78
K_2O	8.39	8.49	7.90	7.23	7.14	6.70	6.65	6.81	0.02	0.03	0.04	0.00	0,01	0.04	1.89
Total	94.69	95.12	96.59	97.40	94.54	95.00	95.04	93.54	88.55	88.93	90.15	97.61	99.09	101.45	92.61
Si	2.672	2.617	2.720	2.665	2.719	2.768	3.066	3.252	2.548	2.598	2.539	8.495	7.695	2.841	6.324
Al IV	1.138	1.383	1.280	1.335	1.281	1.232	0.934	0.748	1.452	1.402	1.461	0.000	0.305	1.160	6.000
Al VI	0.570	0.423	0.264	0.218	0.247	0.250	1.950	1.869	1.107	1.143	1.169	16.103	17.191	0.000	1.315
Ti	0.068	0.079	0.091	0.095	0.089	0.082	0.020	0.017	0.012	0.006	0.008	0.164	0.128	0.000	0.004
Fe^{3+}	0.168	0.170	0.168	0.180	0.171	0.178	0.033	0.022	0.322	0.247	0.279	0.000	0.000	0.004	0.000
Fe^{2+}	0.950	0.963	0.952	1.019	0.968	1.009	0.014	0.033	1.618	1.655	1.656	3.533	3.140	0.000	0.051
Mn	0.000	0.001	0.000	0.000	0.000	0.003	0.000	0.000	0.003	0.007	0.002	0.000	0.000	0.000	0.005
Mg	1.341	1.259	1.461	1.509	1.506	1.443	0.051	0.105	2.929	2.933	2.876	0.929	0.946	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.002	0.003	0.006	0.003	0.161	0.103
Na	0.017	0.017	0.050	0.017	0.033	0.068	0.215	0.147	0.000	0.000	0.000	0.119	0.000	0.814	1.071
K	0.802	0.809	0.739	0.672	0.681	0.636	0.552	0.572	0.003	0.004	0.005	0.000	0.003	0.002	0.352
Cat.	7.730	7.727	7.726	7.715	7.698	7.670	6.838	6.769	10.000	10.000	10.000	29.349	29.424	4.984	15.226
O	12	12	12	12	12	12	12	12	18	18	18	48	48	8	31
X_{Fe}	0.415	0.433	0.395	0.403	0.383	0.412	-	-	0.356	0.361	0.365	0.792	0.768	-	-
X_{Mg}	0.585	0.566	0.605	0.597	0.596	0.588	-	-	0.644	0.639	0.635	0.208	0.232	-	-

Table 3

Thermocalc P-T results from quartz-mica schists to the south of the village Oreshnik, Sakar Mountain. Abbreviations of end*members* according to Kretz (1983). *Cel Celadonite; East* Eastonite; *Clin Clinochlore; Daph Daphnite; Ames Amessite; Mst Mg-staurolite; Fst Fe-staurolite, NR – number of independent reactions, e.e.m. – eliminated end members,* σ – standart deviation (*activities were calcula*ted with the program aX.2000)

	9-1 rim	9-1 core	9-5-1 rim	9-5-1 core	9-5-2 rim	9-5-2 core	9-6 rim	9-6 core
activities								
garnet								
Prp	0.002900	0.001130	0.00530	0.00310	0.00310	0.00310	0.00550	0.00178
Grs	0.000260	0.000400	0.00109	0.00130	0.00051	0.00130	0.00128	0.00160
Alm	0.400000	0.330000	0.34000	0.32000	0.36000	0.32000	0.34000	0.29000
white mica								
Ms	0.60000	0.60000	0.60000	0.60000	0.60000	0.60000	0.60000	0.60000
Pg	0.70000	0.70000	0.70000	0.70000	0.70000	0.70000	0.70000	0.70000
Cel	0.02500	0.02500	0.02500	0.02500	0.02500	0.02500	0.02500	0.02500
biotite								
Phl	0.04600	0.05800	0.07000	0.07000	0.06700	0.07500	0.06700	0.06700
Ann	0.01800	0.01900	0.02200	0.01900	0.02400	0.02000	0.01900	0.01900
East	0.07900	0.07700	0.07200	0.06900	0.05900	0.07100	0.06500	0.06500
chlorite								
Clin	0.05000	0.05900	0.05600	0.05900	0.05600	0.05900	0.05600	0.05900
Daph	0.00360	0.00380	0.00340	0.00380	0.00340	0.00380	0.00340	0.00380
Ames	—	—	0.07800	0.08100	0.07800	0.08100	0.07800	—
plagioclase								
An	0.35000	0.35000	0.35000	0.35000	0.35000	0.35000	0.35000	0.35000
Ab	0.79000	0.79000	0.79000	0.79000	0.79000	0.79000	0.79000	0.79000
staurolite								
Mst	0.00290	0.00190	0.00290	0.00190	0.00290	0.00190	0.00290	0.00190
Fst	0.35000	0.39000	0.35000	0.39000	0.35000	0.39000	0.35000	0.39000
other	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O	Qtz,H_2O
Results								
T^{0}C	**626**	**612**	**616**	**608**	**608**	**609**	**616**	**628**
σ(T)	21	23	21	23	22	23	22	24
P kbar	**7.4**	**7.1**	**7.8**	**7.7**	**7.1**	**7.7**	**8.0**	**7.9**
σ(P)	1.2	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Corr.	0.542	0.555	0.484	0.496	0.507	0.496	0.479	0.671
Fit	1.27	1.38	1.46	1.55	1.50	1.54	1.49	1.50
NR	9	9	10	10	10	10	10	9
e.e.m.	ames	ames	—	—	—	—	—	ames

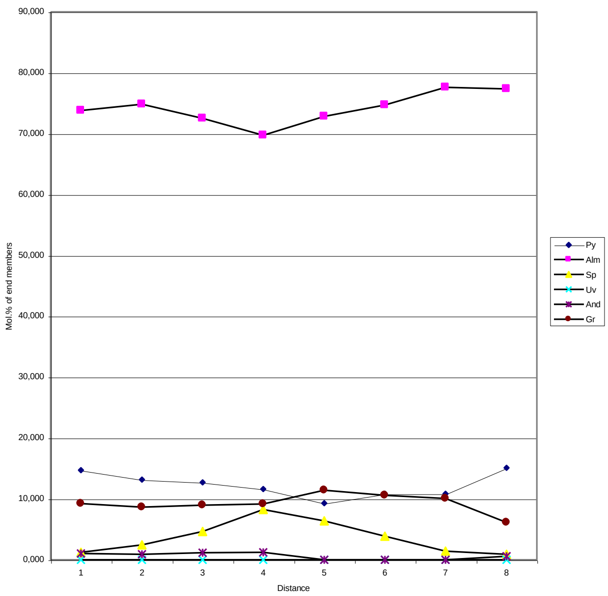

Fig. 3. Garnet profile. Distance 1 DIV = 2 microns

The garnet-biotite geothermometry of core-core analyses give lower temperature than rim-rim analyses of the same garnet grain (see Fig. 4). The lines 1 and 3 indicate the temperature of the garnet core – biotite core Fe-Mg exchange reaction

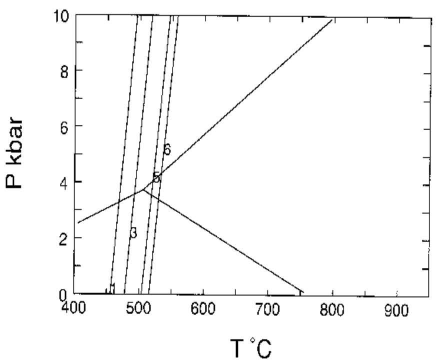

Fig. 4. Garnet–biotite Fe-Mg exchange callibration by Perchuk & Lavrenteva (1984); 1–3 garnet core - biotite core, 5-6 garnet rim – biotite rim

(calibration of Perchuk & Lavrenteva - 1984). It is about 450-470^0 C. The lines 5 and 6 show the temperature of the garnet rim - biotite rim Fe-Mg exchange which is about 500-540^0 C. Hence the cores seemed to have formed at lower temperatures than the rims. This can be explained with garnet growth during prograde metamorphic reactions, when metamorphic temperatures increased. The Thermocalc P-T results from quartz-mica schists to the south of the village Oreshnik, Sakar Mountain are shown at Table 3. The average temperature is calculated 615^0 C, σ (T) = 22,375 and the average pressure – 7,6 kbars, σ (P) = 1,29. This P-T conditions determined lower amphibolite facies (Bucher, Frey, 2002). The garnet-biotite geothermometers show lower temperature than geothermometers, which include staurolite. Be based on the quantity of the minerals and interrelations between them and on the temperatures of the geothermometers involving biotite and garnet, and biotite, garnet and staurolite can be made supposition that the order of the appearance of the minerals in the rock in terms of increasing of the temperature is: chlorite → biotite and garnet → staurolite.

Conclusions

The garnets are almandine rich and common form appears to be {110}. All studied garnets are one-phase and continuously zoned. The order of the appearance of the minerals in the rock in therms of increasing temperature is: chlorite → biotite and garnet → staurolite. The metamorphic grade of the studied rocks is of a low amphibolite facies.

Acknowledgements. I wish to express my thanks to Assoc. Prof. Dr. R. I. Kostov and to Dipl. Geol. N. Gospodinov for taking part in the collection of the samples. Prof. J. G. Raith`s (University of Leoben) help is greatfully acknowledged. This research has been performed with the financial help of the Program for students mobility "Erasmus-Socrates" in the University of Leoben, Austria.

References

Boyanov, I., D. Kozhoukharov, S. Savov. 1965. Geological structure of the southern slopes of the Sakar Mountain between villages Radovetz and Kostur. – *Rev. Bulg. Geol. Soc.*, *26*, 2, 121-134.

Bucher, K., M. Frey. 2002. *Petrogenesis of Metamorphic Rocks.* Springer-Verlag, Berlin – Heidelberg.

Čatalov, G. 1985. Contribution to the stratigraphy and lithology of Sakar-type Triassic (Sakar Mountain, south-east Bulgaria). – *Rev. Bulg. Geol. Soc.*, *46*, 2, 127-143.

GTB. Program Thermobarometry version 2.1 by Frank S. Spear and Matthew J. Kohn. 2001.

Kostov, I., V. Breskovska, J. Mincheva-Stefanova, G. Kirov. 1964. *The Minerals of Bulgaria*. Sofia, Bulgarian Acad. Sci., 261-268 (in Bulgarian).

Kozhoukharov, D. 1996. Lithostratigraphy of the metamorphic triassic of the Lissovo Graben, South Sakar, Svilengrad district. – *Compt. Rend. Acad. Bulg. Sci.*, *49*, 7-8, 89-92.

Kozhoukharov, D., I. Boyanov, S. Savov. 1968. Geology of the region between village Klokotnitza and Maritza town, Haskovo district. – In: *Jubilee Geological Collection.* Geological Institute, BAS, Sofia, 37-50.

Kretz, R. 1983. Symbols for rock-forming minerals. – *Amer. Mineralogist, 68*, 277-279.

Mineral activity calculations for thermobarometry aX, by Tim Holland and Roger Powell, 2000.

Thermocalc 3.1 by Roger Powell and Tim Holland. 2001.

Tracy, R. J. 1985. Compositional zoning and inclusions in metamorphic minerals. – In: *Reviews in Mineralogy*, *10*, Mineralogical Society of America, 355-397.

Recommended for publication by Department of
Mineralogy and Petrology, Faculty of Geology and Prospecting