Доклади на Българската академия на науките
Comptes rendus de l'Académie bulgare des Sciences

Tome 59, No 5, 2006

GEOLOGIE
Mineralogie

CRYSTAL CHEMICAL FEATURES OF GARNETS FROM METAMORPHIC ROCKS OF ZHALTI CHAL AND USTREM FORMATIONS FROM THE FRAME OF SAKAR PLUTON, SE BULGARIA

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(*Submitted by Corresponding Member I. Velinov on March 15, 2006*)

Abstract

To elucidate the garnet forming processes and their relation to the metamorphism in the rim of the Sakar pluton (SE Bulgaria) the crystal chemical features of garnets (chemical composition, admixtures, unit cell parameter and compositional zoning) in metamorphic rocks of Zhalti Chal and Ustrem Formations are studied. The garnets are almandine rich. For the samples from Zhalti Chal Formation the molar percentages of almandine are in the range 70.23–78.96, of grossular – 4.24–16.53, of pyrope – 5.01–13.97 and of spessartine – 3.56–11.37. For the samples from Ustrem Formation the molar percentages of almandine are in the range 72.67–74.76, of grossular – 9.83–14.46, of pyrope – 8.02–10.37 and of spessartine – 3.20–6.44. The values of the unit cell parameter of the garnets from Zhalti Chal Formation range from 11.544 to 11.597 Å while those from the Ustrem Formation – from 11.552 to 11.583 Å. The oxide ratio (FeO+MgO)/(CaO+MnO) and the unit cell parameter of the garnets show that the samples from Zhalti Chal Formation formed in more variable P-T conditions of metamorphism compared to the samples from Ustrem Formation. The zoning paths of all studied garnets, except sample 2, are of the normal type characterizing a prograde genesis. Retrograde features were observed only in the garnet rims. Examination of the growth zoning of sample 2 reveals a complex compositional zoning – indication for growth under polymetamorphic conditions.

Key words: garnet, chemical composition, unit-cell parameter, zoning, metamorphism, Sakar

Introduction. Garnets are nesosilicates with unit cell of eight $X_3Y_2Z_3O_{12}$ formula units. These minerals are interesting because of their chemical variability due to ability of the garnet structure to accommodate divalent, trivalent and tetravalent cations. The thermobarometric features of metamorphic garnets in solid-solid equilibrium are very important. Most mineralogical equilibria used as geothermometers and geobarometers involve garnet as one of the phases. The specific combination of growth and volume diffusion characteristics of garnet makes it unique as a tool for studying the kinetic processes in metamorphic rocks [1].

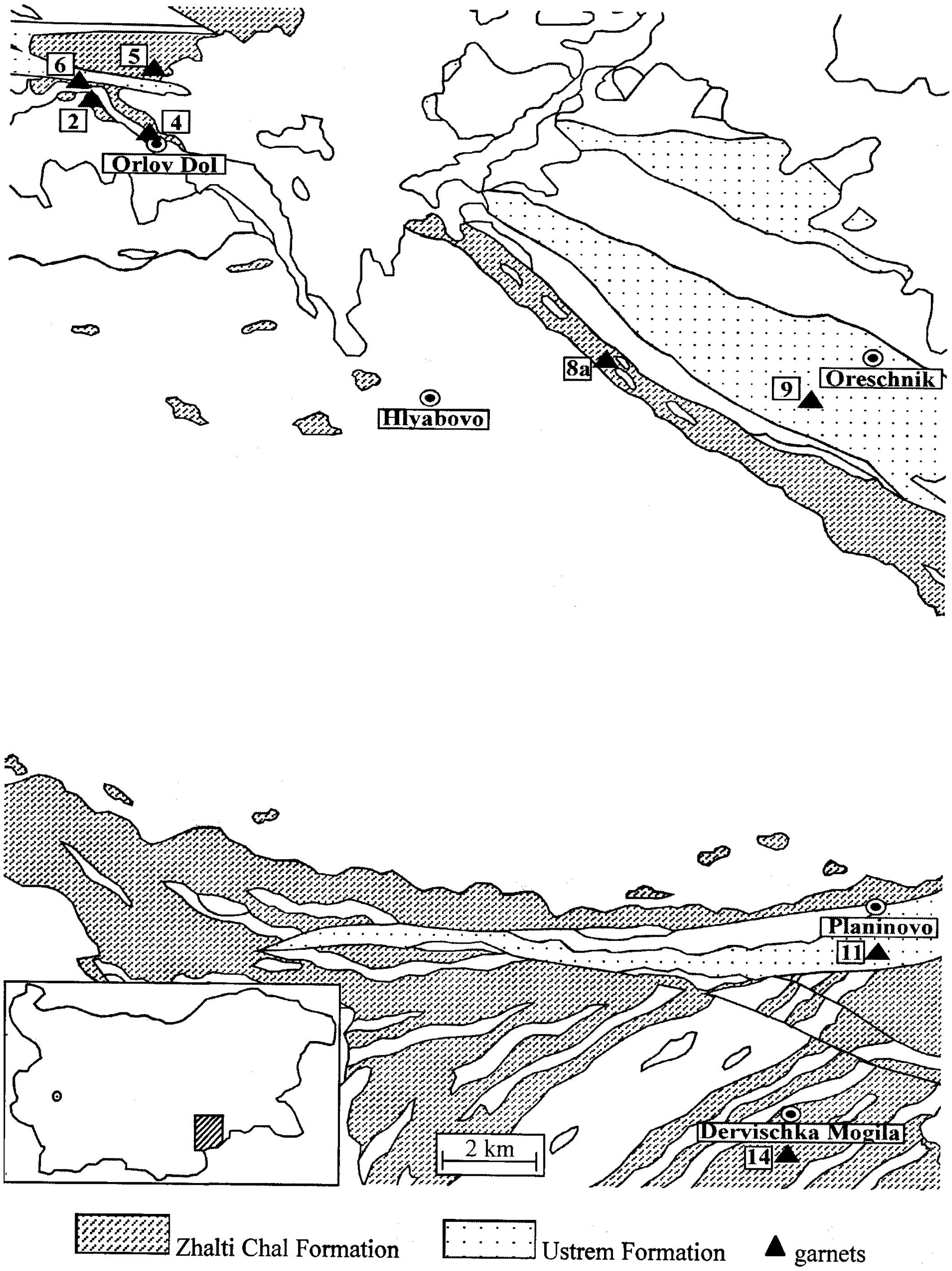

Fig. 1. Location of the studied garnet samples from metamorphic rocks of Zhalti Chal and Ustrem Formations surrounding the Sakar granite pluton (SE Bulgaria)

The aim of the paper is to provide data on the crystal chemistry (unit-cell parameter, chemical composition, admixtures and growth zoning) of garnets from the metamorphic rocks of Zhalti Chal and Ustrem Formations surrounding the Sakar granite pluton. Such data can be used for studying the indicative features of garnets, including crystal morphology, chemical composition and physical properties which are related to the mineral forming processes. Investigation of the garnet mineralogy can help to clarify the garnet forming processes and their relation to metamorphism in the studied region. Up to now studies were performed on garnets from the region of the town of Topolovgrad [2, 3] and near the village of Lessovo [4].

Geological notes. Sakar Mountain is situated in SE Bulgaria. Sakar unit is part of the Strandzha-Sakar zone in the Srednogorie morphotectonic unit. The main magmatic body in Sakar unit is the Sakar granite pluton, intruded in the metamorphic rocks of the Prerhodopian Supergroup. Zhalti Chal Formation (ZhChF) is part of the Prerhodopian Supergroup of East Rhodope Mountains (KOZHOUKHAROV [5]). The rocks from ZhChF are of amphibolite facies [6] and in the eastern part of the Sakar unit (village Lessovo) they are of epidote-amphibolite facies [4].

The lithostratigraphic dismemberment of the metamorphic Triassic includes the metamorphic rocks in the Topolovgrad Supergroup, subdivided into Paleokastro, Ustrem and Srem Formations. The rocks of Ustrem Formation (UsF) [7, 8] are of upper Lower Triassic age. The rocks of Topolovgrad Group are suggested to have undergone metamorphism into amphibolite [8] or epidote-amphibolite [9] facies.

Sampling. The places of sampling are near the villages of Orlov Dol (samples 2, 4, 5 and 6), Hlyabovo (8), Oreschnik (9), Planinovo (11b, 11a, 12 and 13) and Dervischka Mogila (14) (Fig. 1). Samples 2, 4, 5, 6, 8, and 14 were taken from the metamorphic rocks of ZhChF, which are two-mica schists with lepidogranoblastic texture, with apparent garnet porphyroblasts. They are composed of muscovite, biotite, quartz, garnet and plagioclase. Accessory minerals are apatite, tourmaline, zircon, titanite, ilmenite, rutile and calcite. Alteration products are epidote and chlorite [10]. Samples 9, 11a, 11b, 12, and 13 are from the Triassic metamorphic rocks of UsF. The host rocks are fine-grained two-mica schists, granolepidoblastic and porphyroblastic due to garnet and staurolite. The mineral composition of the host rocks is similar to that of the two-mica schists of ZhChF, except for staurolite and chlorite. The latter mineral was considered as a primary mineral [11]. Sample 11a is from amphibolites near the village of Planinovo. The mineral composition of the host rock is mainly hornblende, quartz and garnet with sporadic titanite, zoisite, chlorite, tourmaline, rutile, plagioclase, zircon and ore mineral.

Methods. The chemical composition of the samples was studied by AES ICP analysis. Powder X-ray diffraction (XRD) analysis of the garnets was performed by DRON 3M diffractometer in the range 20–80°2θ (Fe-filtered Co-K$_\alpha$ radiation, 40 kV, 28 mA). A step-scan technique was applied (step 0.02°2θ, 3 s per step). The unit cell parameter, a, of the garnets was refined using Rietveld based software – the programme Fullprof [12], which allows high precision of calculation of a as the aim is not only to determine the nature of garnet but also to find differences in the unit cell parameter of garnets with varying chemical compositions. The structure data for almandine of ARMBRUSTER et al. [13] was used to generate the theorethical powder pattern needed for the calculations. The obtained values of a were used for unit cell volume and density calculations. The chemical zoning of the minerals was studied with electron microprobe analyses (ARL-SEMQ S30, 4 spectrometers, EDS Link, 20 KV, 20 nA).

Results and discussion. The powder XRD patterns of the investigated garnets correspond to that of almandine (ICDD-PDF No33-0658). To compare the crystal chemical features and to clarify better the geological conditions in which the garnets were formed, the values of a, unit cell volumes and densities of the samples from the

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Values of the oxide ratio (FeO+MgO)/(CaO+MnO), mean radius of the X-cations r{X}, mean radius of the Y-cations r{Y}, unit cell parameter a_0 (Å), cell volume V (Å^3) and density D (g/cm^3) of studied garnets from Zhalti Chal and Ustrem Formations (Sakar Mountain)

Formation	No	(FeO+MgO)/(CaO+MnO)	r{X}	r{Y}	X_{Ca}	X_{Mg}	a (Å) obs.	V (Å^3) obs.	D (g/cm^3) obs.
Zhalti Chal	6	3.52	0.955	0.540	0.165	0.053	11.597 (3)	1559	4.109
	5	5.25	0.950	0.540	0.149	0.050	11.578 (4)	1552	4.124
	8	6.37	0.935	0.538	0.086	0.140	11.558 (3)	1544	4.059
	14	7.28	0.931	0.539	0.053	0.083	11.544 (4)	1538	4.172
Ustrem	13	5.62	0.947	0.538	0.140	0.080	11.583 (3)	1554	4.002
	11	5.28	0.947	0.538	0.139	0.095	11.581 (3)	1553	3.995
	12	5.30	0.948	0.539	0.145	0.081	11.575 (3)	1550	4.020
	9	5.64	0.939	0.538	0.098	0.104	11.552 (3)	1541	4.052

two metamorphic formations are calculated (Table 1). As it is seen from Table 1 the values of a of the garnets from ZhChF range from 11.544 to 11.597 Å and those from UsF– from 11.552 to 11.583 Å. The parameter increases more significantly with the increase of the mean radius of the cations in the octahedral position (X-cations) of the structure than with increasing of the mean radius of the cations in hexahedral (Y-cations) coordination, calculated using the effective radii of SHANON [14, 15]. As a rule, in garnets the increase of X_{Ca} along with decrease of X_{Mg} leads to increase of a [16]. Relation between the values of a of the studied garnets and X_{Mg} was not observed. In all samples, except sample 12, increase in X_{Ca} leads to increase in a. The a parameter of garnet depends mainly on the isomorphic admixtures in the garnet structure. In this sense further studies on sample 12 are necessary.

The calculated densities of garnets from ZhChF range from 4.059 to 4.172 g/cm^3 and of those from UsF – from 3.995 to 4.052 g/cm^3 (Table 1).

Based on AES ICP analysis the garnets are a solid solution in the almandine – grossular – pyrope – spessartine quaternary system (Table 2). All they are almandine-rich with varying amounts of other end members. A larger variation is observed in the molar percentages of the end members of the samples from ZhChF compared to UsF. For samples from ZhChF the molar percentages of almandine are in the range 70.23–78.96, of grossular – 4.24–16.53, of pyrope – 5.01–13.97 and of spessartine – 3.56–11.37. For samples from UsF these percentages are in the ranges: for almandine – 72.67–74.76, for grossular – 9.83–14.46, for pyrope – 8.02–10.37 and for spessartine – 3.20–6.44. The presence of the end members of the studied garnets from UsF follows the row: Alm > Grs $\gtreqless$ Prp > Sps. No quantitative dependence was observed between grossular, pyrope and spessartine end members in the samples from ZhChF. The larger chemical variation in the garnets from the metamorphic rocks of ZhChF compared to this in the garnets of UsF is indicative of larger variation in the whole-rock chemistry of the host rocks and their protoliths.

For Ca-poor garnets in regional metamorphic rocks the ratio (FeO+MgO)/(CaO+MnO) is known to be sensitive for the metamorphic grade. The increase of this ratio is an indicator for rise in metamorphic grade along with decrease of a. These ratios are also related to variations in pressure [17]. As it is seen in Table 1, garnets from the rocks of UsF are characterized by similar oxide ratio, which is indicative of their formation in close P-T conditions of metamorphism. The garnets from ZhChF differ from the latter with large variation in their oxide ratio. The narrow intervals in oxide ratio values and unit cell parameter variations for the samples from ZhChF are indicative of small

Table 2

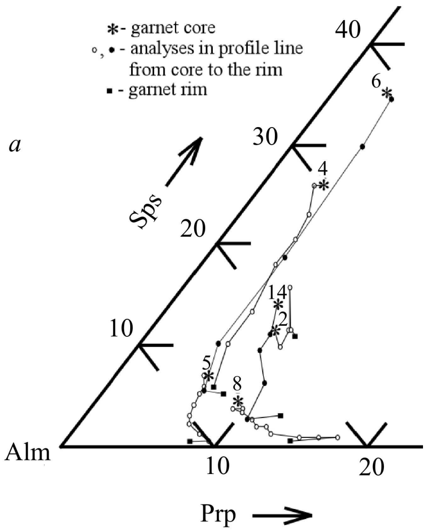
AES ICP analysis of garnets from Zhalti Chal (No 2, 4, 5, 6, 7, 8, 14) and Ustrem (No 9, 11b, 12, 13) Formations surrounding the Sakar granite pluton (SE Bulgaria). Abbreviations of end members according to Kretz (1983). $X_{Mg} = Mg/(Fe^{2+} + Mg + Mn + Ca)$, $X_{Ca} = Ca/(Fe^{2+} + Mg + Mn + Ca)$

Oxides wt%	2	4	5	6	8	9	11b	12	13	14
SiO_2	36.46	35.61	33.84	33.75	35.65	37.16	39.35	38.64	39.32	33.77
TiO_2	0.47	0.72	1.14	1.25	0.67	0.75	0.60	0.80	0.76	0.87
Al_2O_3	19.87	19.72	20.01	20.18	20.59	20.42	18.76	18.67	18.57	20.59
Fe_2O_3	32.78	35.85	36.32	33.82	33.31	32.93	32.27	33.24	33.41	37.18
MnO	4.22	4.61	1.50	3.41	2.41	2.57	1.55	1.42	1.27	3.12
MgO	1.86	1.34	1.20	1.28	3.28	2.35	2.12	1.85	1.81	1.97
CaO	3.39	1.36	4.95	5.59	2.81	3.10	4.35	4.57	4.40	1.75
Na_2O	0.06	0.04	0.04	0.05	0.63	0.05	0.04	0.05	0.03	0.05
K_2O	0.14	0.06	0.06	0.05	0.09	0.09	0.16	0.10	0.12	0.04
Total	99.25	99.31	99.06	99.38	99.44	99.42	99.20	99.34	99.69	99.34
Numbers of cations on the basis of 12 oxygens										
Si	3.048	3.018	2.890	2.865	2.963	3.066	3.227	3.188	3.224	2.879
Al	0.000	0.000	0.110	0.135	0.037	0.000	0.000	0.000	0.000	0.121
Ti	0.030	0.046	0.073	0.080	0.042	0.047	0.037	0.050	0.047	0.056
Al	1.958	1.970	2.014	2.019	2.017	1.986	1.813	1.815	1.795	2.069
Fe^{2+}	2.062	2.286	2.333	2.160	2.083	2.044	1.991	2.063	2.061	2.385
Mn	0.299	0.331	0.108	0.245	0.170	0.180	0.108	0.099	0.088	0.225
Mg	0.232	0.169	0.153	0.162	0.406	0.289	0.259	0.228	0.221	0.250
Ca	0.304	0.123	0.453	0.508	0.250	0.274	0.382	0.404	0.387	0.160
Na	0.010	0.007	0.007	0.008	0.102	0.008	0.006	0.008	0.005	0.008
K	0.015	0.006	0.007	0.005	0.010	0.009	0.017	0.011	0.013	0.004
Sum.	7.956	7.957	8.037	8.053	8.042	7.903	7.841	7.865	7.840	8.037
End members:										
Alm	71.20	78.57	76.57	70.23	71.60	73.35	72.67	73.85	74.76	78.96
Grs	10.48	4.24	14.86	16.53	8.60	9.83	13.95	14.46	14.02	5.29
Prp	8.00	5.82	5.01	5.27	13.97	10.37	9.46	8.14	8.03	8.29
Sps	10.32	11.37	3.56	7.97	5.83	6.44	3.93	3.55	3.20	7.46
X_{Mg}	0.08	0.06	0.05	0.05	0.14	0.10	0.09	0.08	0.08	0.08
X_{Ca}	0.10	0.04	0.15	0.17	0.09	0.10	0.14	0.14	0.14	0.05

differences in the P-T conditions of metamorphism under which the garnets near the villages of Orlov Dol, Hlyabovo and Dervishka Mogila were formed.

Using AES ICP analysis the admixtures determined in the garnets from ZhChF are: P_2O_5 (0.03–0.19 wt%), SO_3 (0.03–0.37 wt%), Ba (10–92 mg/kg), Co (10–18 mg/kg), Cr (63–128 mg/kg), Ni (10–40 mg/kg), Sr (17–36 mg/kg), V (56–115 mg/kg), Zn (108–218 mg/kg), Zr (15–31 mg/kg). The admixtures in garnets from UsF are in narrower ranges: P_2O_5 (0.07–0.20 wt%), SO_3 (0.03–0.28 wt%), Ba (13–15 mg/kg), Co (10–18 mg/kg), Cr (81–102 mg/kg), Ni (10–27 mg/kg), Sr (6–19 mg/kg), V (59–113 mg/kg), Zn (104–179 mg/kg), Zr (16–30 mg/kg).

The compositional (growth) zoning in garnets was studied by spot microprobe analyses at equal distance in a core-rim profile line. The Prp-Alm-Sps ternary diagrams (Fig. 2) show the trends in the growth-zoned garnets from the rocks of ZhChF and UsF. Advantage of such diagrams is that they may be used for elucidation of the reactions of garnet formation as well as of changes in the reactant assemblage. Sample 2 shows



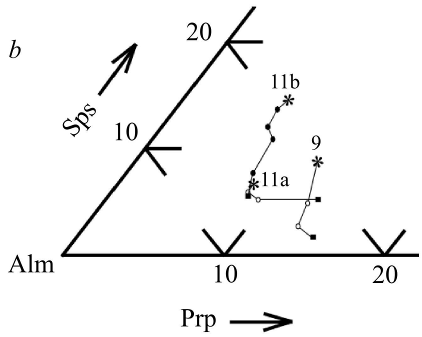


Fig. 2. Almandine-pyrope-spessartine (in mol.%) ternary plot, showing zoning paths of garnets form: *a*) Zhalti Chal Formation; *b*) Ustrem Formation. The numbers of the samples are marked near their core analyses

a complex growth zoning (Fig. 2). At the beginning of its growth the normal type of compositional zoning is observed and shows increase in FeO and MgO and decrease in MnO in core-to-rim direction. The normal type of zoning is of prograde genesis and well documented for minerals, which were grown with the increase of temperature [18]. Then the zoning trend is kinked to the reverse direction. MnO contents increase from core to rim, along with decrease in FeO and MgO contents, thus demonstrating the reverse type of zoning. The last is of retrograde genesis. It is a typical feature of minerals grown during decrease of temperature. As it is seen in Fig. 2, the zoning path of the garnet is kinked once again and the reverse type of zoning is changed to normal type of zoning. The study of the growth zoning features of sample 2 allows one to suggest garnet formation in three different reactions caused by a double change in the conditions of metamorphism. Complex compositional zoning is usually observed in garnets grown under polymetamorphic conditions. Other hypotheses of garnet genesis are the metasomatic one (not applicable for garnets sized up to 2 mm, such as sample 2) and the monometamorphic hypothesis, which accepts that garnet can form a complex type of zoning in one metamorphic cycle by involving formation of new minerals during the reaction (not applicable for rocks with "pelitic" chemical composition and empty of other Ca-bearing minerals, except plagioclase and garnet) [18].

The zoning trend in sample 4 shows a constant content of MnO at the beginning of its growth. Then the garnet growth was under conditions of a continuous temperature increase, thus forming a normal type of compositional zoning. Most probably, the smooth and continuous path of sample 4 corresponds to growth during a single reaction.

Samples 6 and 14 show similar trends in their growth zoning. Considering this fact as well as the similarity in the mineral composition of their host rocks one can assume that both crystals were formed in the same reaction. Enrichment in Mg in the rims of both samples is recorded. The zoning trend of sample 14 shows decrease in MnO and FeO in its rim, which is a retrograde growth feature in the end of its formation.

Samples 5 and 8 are characterized by normal type of growth zoning. Increase in Fe in their rims may indicate garnet formation in a new reaction in which the material supplied to the garnet is rapidly depleted in MgO. A weak resorption of the garnet edges accompanied by formation of a more magnesian phase such as chlorite or biotite would drive the garnet composition in such direction [1].

The zoning trends in samples 9 and 11b (UsF) are similar to that in sample 6 (ZhChF). At the beginning of its growth the garnet in sample 11a shows a normal type of growth zoning. Then the trend in its zoning changed to MgO increase. It is possible this to be caused by MnO depletion in the host rock.

Conclusion. The crystal chemical features of the studied almandines from the metamorphic rocks of Zhalti Chal Formation reveal larger variations in chemical composition of the host rocks and their protoliths as well as larger variations in the P-T conditions of metamorphism of these rocks compared to the rocks of Ustrem Formation.

Polymetamorphic conditions of garnet growth are suggested only for sample 2 near Orlov Dol village. The other studied garnets show growth under conditions of increasing temperature, thus forming a normal type of compositional zoning. In their zoning paths retrograde growth features were recorded only in their rims.

Acknowledgements. N. Tzankova thanks R. Kostov and N. Gospodinov for the help during sampling and the Central Research Laboratory "Goechemistry" (University of Mining and Geology) for AES ICP analyses. Microprobe analyses of this research have been performed in the University of Leoben, Austria, in the frame of the Program for students' mobility "Erasmus-Socrates". We thank Prof. Velinov and Dr. M. Tarassov for their careful and constructive reviews.

REFERENCES

[1] Tracy R. Rev. in Min., 1982, **10**, 355–397. [2] Костов И., В. Бресковска, Й. Минчева-Стефанова, Г. Киров. Минералите в България. С., БАН, 1964, 540 с. [3] Костов И. Год. Соф. унив., Прир.-мат. фак., **46**, 1950, № 3, 329–338. [4] Grozdanov L., A. Chatalov. Compt. rend. Acad. bulg. Sci., **48**, 1995, No 5, 51–54. [5] Кожухаров, Д. Geologica Balc., **17**, 1987, No 2, 15–38. [6] Kozhoukharov D., E. Kozhoukharova, L. Grozdanov. Ibid., **7**, 1977, No 3, 104–116. [7] Chatalov G. Compt. rend. Acad. bulg. Sci., **38**, 1985, No 6, 711–714. [8] Чаталов Г. Сп. Бълг. геол. д-во, **46**, 1985, № 2, 127–143. [9] Kozhoukharov D., S. Savov. Compt. rend. Acad. bulg. Sci., **49**, 1996, No 7–8, 89–92. [10] Tzankova N. Ibid., **58**, 2005, No 7, 775–782. [11] Id. Ann. Univ. Min. Geol. "St. Ivan Rilski", **48**, 2005, 155–160. [12] Rodriguez-Carvajal J. FULLPROF: A

Program for Rietveld Refinement and Pattern Matching Analysis, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, 127. [13] Armbruster T., C. Geiger, G. Lager. Amer. Min., 1992, **77**, 512–521. [14] Shanon R., C. Prewitt. Acta Cryst., 1969, **B25**, 925–945. [15] Shanon R. Ibid., 1976, **A32**, 751–767. [16] Deer W., R. Howie, J. Zussman. An introduction to the Rock-Forming Minerals, London, Pearson, 1992, 696. [17] Deer W., R. Howie, J. Zussman. Rock-Forming Minerals. Orthosilicates, A., London, Alden Press, 1997, 913. [18] Авченко О. Петрогенетическая информативность гранатов метаморфических пород, Москва, Наука, 1982, 103.

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