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# ICP AES, microprobe, and X-ray powder diffraction data for garnets from metamorphic rocks in the Sakar region, SE Bulgaria

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**Abstract.** In order to obtain informative data on the crystal chemistry of garnets from metamorphic rocks of the Zhulti Chal and Ustrem Formations in the rim of the Sakar pluton (SE Bulgaria), their chemical composition, trace elements, unit cell parameters and compositional zoning were investigated. All garnets are almandine rich. For samples from the Zhulti Chal Formation the molar percentage of almandine range from 70.2 to 79.0, of grossular – from 4.2 to 16.5, of pyrope – from 5.0 to 14.0 and of spessartine – from 3.6 to 11.4. For samples from the Ustrem Formation the molar percentage of almandine range from 72.7 to 74.8, of grossular – from 9.8 to 14.5, of pyrope – from 8.0 to 10.4 and of spessartine – from 3.2 to 6.4. The values of the unit cell parameter of garnets from the Zhulti Chal Formation range between 11.544(4) and 11.597(3) Å while those from the Ustrem Formation – between 11.552(3) and 11.583(3) Å. The (FeO+MgO) / (CaO+MnO) oxide ratio and the unit cell parameters allow suggesting that samples from the Zhulti Chal Formation were formed in more variable temperature conditions of metamorphism in comparison with samples from the Ustrem Formation.

The following trace elements were determined in the studied garnets: $P_2O_5$ (0.03-0.20 wt.%), $SO_3$ (<0.03-0.37 wt.%), Ba (10-92 ppm), Co (<10-18 ppm), Cr (63-128 ppm), Ni (<10-40 ppm), Sr (6-36 ppm), V (56-115 ppm), Zn (104-218 ppm), Zr (15-31 ppm).

The zoning paths of the studied garnets, except sample No 2, show normal type of compositional zoning. It is of prograde genesis. Only in the garnet rims the retrograde features were observed. The examination of the growth zoning features of sample No 2 from the region of the Orlov Dol village shows complex compositional zoning, which is a possible indication for growth under polymetamorphic conditions.

*Key words:* garnet, chemical composition, trace elements, unit-cell parameter, metamorphism

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**Николета Цанкова, Огнян Петров. ICP AES микросондови и рентгенографски данни за гранати от метаморфните скали в Сакарския район, ЮИ България**

**Резюме.** С цел получаване на информативни данни за кристалохимичните особености на гранати от Жълтичалската и Устремска свити от рамката на Сакарския плутон (ЮИ България) е изследван техният химичен състав, примеси, параметър на елементарна клетка и композиционна зоналност. Всички изследвани гранати са от алмандинов тип. При образците от Жълтичалската свита молните проценти на алмандина варират от 70,2 до 79,0, на гросулара – от 4,2 до 16,5, на пиропа – от 5,0 до 14,0 и на спесартина – от 3,6 до 11,4. За образците от Устремската свита молните проценти на алмандина варират от 72,7 до 74,8, на гросулара – от 9,8 до 14,5, на пиропа – от 8,0 до 10,4 и на спесартина – от 3,2 до 6,4. Параметърът на елементарната клетка на изследваните гранати от Жълтичалската свита показа стойности от 11,544(4) до 11,597(3) Å, докато при гранатите от Устремската свита е в границите от 11,552(3) до 11,583(3) Å. Стойностите на оксидното отношение (FeO+MgO) / (CaO+MnO) и параметрите на елементарната клетка на изследваните гранати, позволяват да се допусне, че образците от Жълтичалската свита са формирани в условия на по-големи вариации в температурата на метаморфизма, в сравнение с образците от Устремската свита.

В изследваните гранати са установени следните примеси: $P_2O_5$ (0,03-0,20 wt.%), $SO_3$ (<0,03-0,37 wt.%), Ba (10-92 ppm), Co (<10-18 ppm), Cr (63-128 ppm), Ni (<10-40 ppm), Sr (6-36 ppm), V (56-115 ppm), Zn (104-218 ppm), Zr (15-31 ppm).

Всички изследвани гранати, с изключение на образец № 2, показват нормален тип композиционна зоналност от проградния стадий. Единствено в периферията на гранатовите порфиробласти се наблюдават ретроградни особености. Изследването на особеностите в зоналността на растеж на образец № 2 от района на с. Орлов дол показва сложен тип зоналност, за която може да се предположи, че е индикация за растеж в условия на полиметаморфизъм.

## Introduction

Garnets are classified as nesosilicates. Their unit-cell contains eight $X_3Y_2Z_3O_{12}$ formula units. The garnets are one of the diagnostic metamorphic minerals and variations in their composition have long been studied as an indicator of metamorphic grade conditions. Such compositional variations that have been detected between and within grains in the same rock strata are usually explained in terms of cationic fractionation with changing temperature during specific continuous reactions involving elemental distribution patterns in the rock matrix around the crystallizing garnet. Garnet compositions are also said to correlate with their metamorphic grade.

The special combination of growth and volume diffusion characteristics of garnet has made it virtually unique as a tool for studying the kinetic processes in metamorphic rocks. Other metamorphic minerals display zoning more rarely, which generally is a result of special conditions such as rapid heating and cooling (Tracy, 1982).

The goal of this paper is to provide data about the crystal chemistry of garnets from metamorphic rocks of the Zhulti Chal and Ustrem Formations from the frame of Sakar pluton – to investigate their unit-cell parameters, chemical composition, trace elements and growth zoning. These data can be used in future for studying the nature of indicative properties of garnets. The indicative features of garnets include peculiarities in crystal morphology, chemical composition and physical properties, all related to the mineral forming processes and conditions. The study of the mineralogy of garnets helps to elucidate the garnet forming processes and their relation to metamorphism in the studied region.

The garnets from the region of Topolovgrad are almandine rich with a notable grossular and pyrope content (Kostov et al., 1964) and a correlation between the garnet crystal size, chemical composition and geological setting has been observed (Kostov, 1950).

Microprobe analyses of garnet from amphibolites in the vicinity of the village of Lessovo show its homogeneous composition including: 73.4 mol. % almandine, 11.3 mol.% grossular, 10.3 mol.% spessartine and 0.5 mol.% pyrope (Grozdanov, Chatalov, 1995).

## Notes on geology

Sakar Mountain is situated in South-East Bulgaria. The Sakar unit is a part of Strandza-Sakar zone in Srednogorie morphotectonic unit. The main magmatic body in the studied district is the Sakar granite pluton, intruded into the metamorphic rocks of the Pre-Rhodopian Supergroup. The Zhulti Chal Formation is a part of the Pre-Rhodopian Supergroup introduced by Kozhoukharov (1987) with a type section to the south of the Zhulti Chal village, East Rhodope Mountains. The Formation is built up of white mica and two-mica schists and gneiss-schists with interbeds of white mica leptynites, amphibolits, graphite-bearing quartzites and different in size complexly boudinaged bodies of metamorphosed ultrabasites, eclogites and gabbroids. The rocks from the Zhulti Chal Formation are of amphibolite facies (Kozhoukharov et al., 1977) and in the eastern part of the Sakar unit (vicinity of the village of Lessovo) of epidote-amphibolite facies (Grozdanov, Chatalov, 1995).

The lithostratigraphic dismemberment of the metamorphic Triassic integrates the metamorphic rocks in the so-called Topolovgrad Supergroup, subdivided into three formations – Paleokastro, Ustrem and Srem Formations. The Paleokastro Formation is built up of metaconglomerates, metasandstones and mica-schists. The Ustrem Formation is represented by quartz-mica schists containing porphyroblasts of biotite, garnet and staurolite; garnet-amphibole, epidote-zoisite and quartz-amphobole schists; calc-schists; white, grey and striped marbles. The Srem Formation is built up of calcic and dolomitic marbles. The rocks of the Ustrem Formation are situated over 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 rocks of the Ustrem Formation are of upper Lower Triassic age. The Ustrem Formation was described by Chatalov (1985a,b) with a type area in the Topolovgrad region. According to mineral paragenesis the rocks of the Topolovgrad Group are suggested to have undergone metamorphism of epidote-amphibolite (Kozhoukharov, Savov, 1996) or amphibolite (Chatalov, 1985b) facies.

## Sampling and rocks

In North to South direction the places of sampling are in the region of the villages Orlov Dol (samples No 2, 4, 5 and 6), Hlyabovo (No 8), Oreschnik (No 9), Planinovo (No 11b, 11a, 12 and 13) and Dervischka Mogila (No 14) (Fig. 1). The mineral composition of host rocks of garnets is shown in Table 1. Samples No 2, 4, 5, 6, 8, and 14 were taken from the metamorphic rocks of Zhulti Chal Formation, represent by two-mica schists with lepidogranoblastic texture, clearly with porphyroblasts of garnet. The rocks 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 (Tzankova, 2005a,b).

Samples No 9, 11a, 11b, 12, and 13 were taken from the Triassic metamorphic rocks of the Ustrem Formation. The rocks are fine-grained two-mica schists, granolepidoblastic and porphyroblastic due to garnet and staurolite. The mineral composition of these rocks is similar to that of the studied two-mica schists of Zhulti Chal Formation, except for staurolite and chlorite. The latter mineral was considered here as primary mineral (Tzankova, 2005b). Sample No 11a was taken from the amphibolites near Planinovo village. The rock

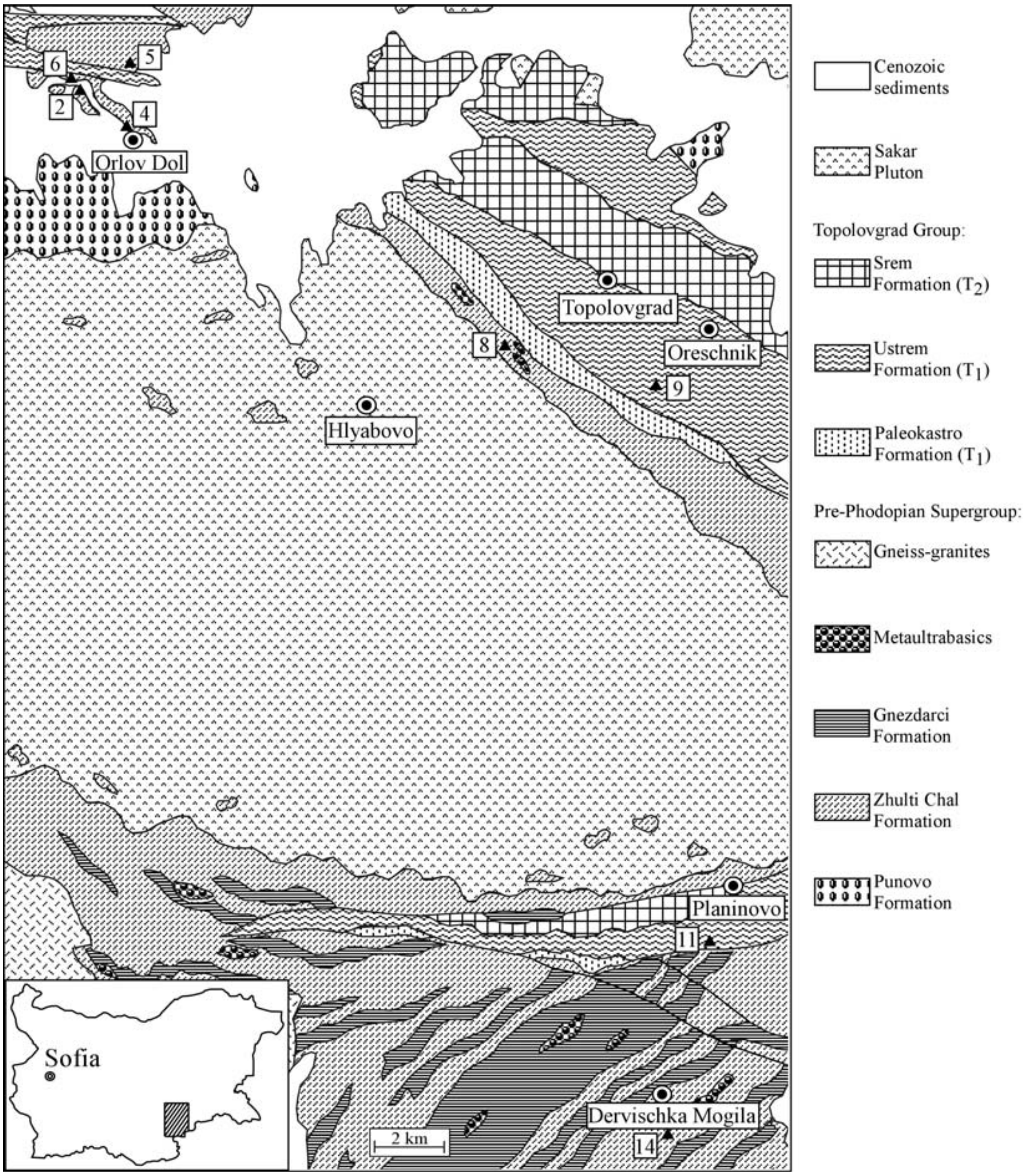


Fig. 1. Location of the studied garnet samples (▲) from the metamorphic rocks of the Zhulti Chal and Ustrem Formations (after the Geological map of Bulgaria M 1 : 100 000, Kozhoukharov et al., 1994; 1995, simplified)

Фиг. 1. Местонахождение на изследваните гранатови образци (▲) от метаморфните скали от Жълтичалска и Устремска свити (по Геоложката карта на България в М 1: 100 000, Kozhoukharov et al., 1994; 1995)

Table 1. *Mineral composition of metamorphic rocks from the Zhulti Chal  and Ustrem Formations*

Таблица 1. *Минерален състав на изследваните метаморфни скали от Жълтичалска и Устремска свити*

| No | Grt | Ms | Bt | Qtz | Chl | Pl | Ilm | St | Tur | Ap | Ttn | Rt | Hbl | Cal | Zrn | Ep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zhulti Chal Formation – two-mica schists | | | | | | | | | | | | | | | | |
| 2 | N | M1 | M1 | M1 | $S_{Grt, Bt}$ | N | N1 | | A | A | | | | | | |
| 4 | M | M | M | M1 | $S_{Bt}$ | N | N | | | A | | | | A | | |
| 5 | M | M1 | N | M1 | $S_{Grt}$ | N | N1 | | A1 | | A | 1 | | | | |
| 6 | M | M | N | N | A | N | N | | | | A1 | | | A | | $S_{Grt}$ |
| 8 | M | M 1 | M | M1 | $S_{Grt, Bt}$ | N | N1 | | | | | | | A | | |
| 14 | M | M1 | M | M1 | $AS_{Bt}$ | N | N1 | | A | A | | | | 1 | A | 1 |
| Ustrem Formation – two-mica schists, except of No 11a - amphibolite | | | | | | | | | | | | | | | | |
| 9 | M2 | M | M2 | M12 | $AS_{Bt}$ | N | 2 | M | | | | | | A | | |
| 11a | N | | | M1 | A | M | N1 | | 1 | | A | A | M1 | 1 | A | 1 |
| 11b | M | M | M2 | M12 | A2 | N | N12 | M1 | 12 | | | | | | | |
| 12 | M | M1 | M | M12 | A | N | 1 | M | A | | | | | | | |
| 13 | M | M1 | M | M12 | $S_{St}$ | N | N | M | A | A | | | | | | |

*Rock-forming minerals: M - main, N - minor, A - accessory, and their alteration products (S); inclusions: 1 - in garnet, 2 -  in staurolite*

Скалообразуващи минерали: М - главни, N – второстепенни, А – аксесорни, и техните променителни продукти (S); включения: 1 – в гранат, 2 – в ставролит

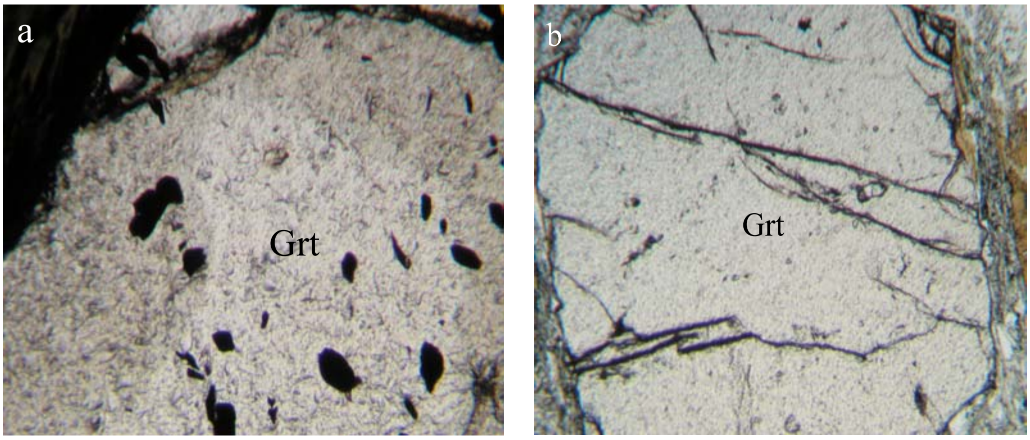


Fig. 2. Microphotographs of garnets: a) sample from the region of the Hlyabovo village (Yavuz Dere) with dark peripheral zones; b) homogeneous crystal from the region of the Oreschnik village without dark sections. Width of the photos 1.04 mm, // N

Фиг. 2. Микроскопски снимки на гранати: а) образец от района на с. Хлябово (Явуздере) с тъмни участъци в периферни зони; б) хомогенен образец от района на с. Орешник. Ширина на снимките – 1, 04 mm, // N

consists mainly of hornblende, quartz and garnet and sporadically of titanite, zoisite, chlorite, tourmaline, rutile, plagioclase, zircon and ore mineral (Table 1).

The growth zoning in the garnets is not visible under the microscope study. However in some of the samples dark sections in their periphery was observed (Fig. 2). The determination of the spatial variation of composition within mineral grains is possible only by using electron probe microanalyses. The type of zoning is directly dependent on the temperature of garnet growth and therefore it is informative about the temperature at which the host rock has been metamorphosed, e.g. up to or above the amphibolite facies. The normal type of zoning does not occur in garnets, which are metamorphosed in grades higher than the amphibolite one. The type of zoning indicates temperature changes during garnet growth as well as retrograde processes. To a certain extent the garnet zoning can be informative about acts of metasomatism.

## Experimental methods

Powder X-ray diffraction (XRD) analyses of the samples were performed on DRON 3M diffractometer with a horizontal Bragg-Brentano goniometer, using Fe-filtered Co-$K_\alpha$ radiation (40 kV, 28 mA). A step-scan technique was applied with a step of 0.02$^o$ 2θ and 3 s per step in the range 20-80$^o$ 2θ. The peak intensities are determined by their integral area, using the program WinFit 1.2.

The chemical compositions of the same samples were studied by Inductively Coupled Plasma with Atom Emission Spectrometry (ICP AES).

The unit cell parameter (*a*) was determined using Rietveld based software – the program Fullprof (Rodriguez-Carvajal, 1990). This program gives precise enough values of *a* and allows finding out differences in the values of the unit cell parameter in garnets with varying chemical compositions. The structure data for almandine of Armbruster et al. (1992) was used to generate the powder pattern needed for the calculations. The exact measured unit cell parameter of the garnets was used for cell volume and density calculations.

The spatial variation of the chemical composition of the minerals was studied with electron microprobe analyses (ARL-SEMQ S30, 4 spectrometers, EDS Link, 20 KV, 20 nA).

The abbreviations of the minerals and their end members are according to Kretz (1983): albite - Ab, almandine - Alm, anorthite - An, apatite - Ap, biotite - Bt, calcite - Cal, chlorite - Chl, epidote - Ep, garnet - Grt, grossular - Grs, hornblende - Hbl, ilmenite - Ilm, muscovite - Ms, plagioclase - Pl, pyrope - Prp, quartz - Qtz, rutile - Rt, spessartine - Sps, staurolite - St, titanite - Ttn, tourmaline - Tur, zircon - Zrn.

## Results and discussion

The XRD powder patterns of the investigated garnets correspond to this of almandine (ICDD-PDF No 33-0658) (Table 2). However, there are some intensity changes of certain peaks, which are informative (Fig. 3).

The intensities $I_{332}$ and $I_{420}$ cannot be affected by the composition of the Y-sites and the intensity ratio $I_{332}/I_{420}$ is indicative for the almandine quantity, while the intensity ratio $I_{642}/I_{332}$ is informative for the the pyrope quantity in Alm-Prp-Grs garnets (Chmielova et al., 1997). According to the crystal data of Armbruster et al. (1992) for end member garnets the following dependence $I_{332} < I_{432} \Rightarrow X_{Alm} < X_{Py}$ exists. Also, the intensity ratio $I_{444}/I_{620}$ is relevant to the quantity of Al in Y position (Encheva et al., 2004). The peak 620 reflecting the presence of $Fe^{3+}$ was not observed in the studied garnets.

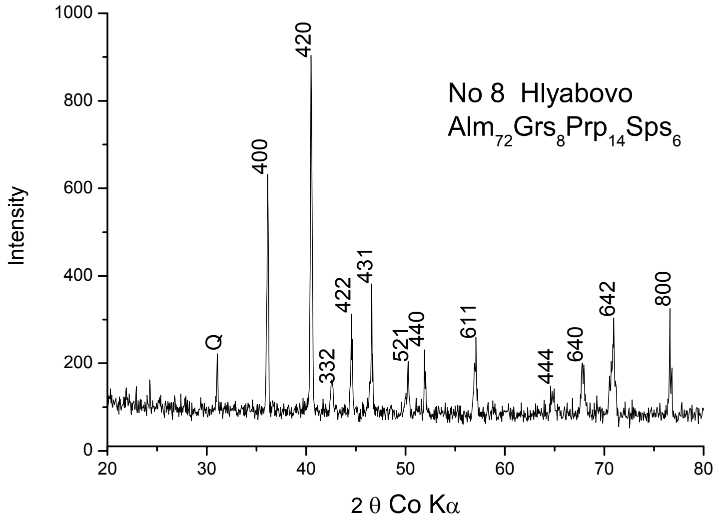


Fig. 3. X-ray powder-diffraction patterns of sample No 8 from the region of the Hlyabovo village (Yavuz Dere)

Фиг. 3. Рентгенова дифрактограма на образец № 8 от района на с. Хлябово (Явуздере)

Table 2. *Interplanar spacing (d) and intensity (I) of X-ray diffractograms of garnets from metamorphic rocks from Zhulti Chal and Ustrem Formations*

Таблица 2. *Междуплоскостни разстояния (d) и интензитети (I) от рентгенови дифрактограми на гранати от метаморфните скали от Жълтичалската и Устремска свити*

| ICDD No 33-0658 | | | Zhulti Chal Formation | | | | | | | | | | | | Ustrem Formation | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2 | | 4 | | 5 | | 6 | | 8 | | 14 | | 9 | | 11b | | 12 | | 13 | |
| d (Å) | I | hkl | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I |
| 4.73 | 8 | 211 | 4.73 | 3 | 4.71 | <1 | 4.72 | 3 | 4.72 | 5 | 4.72 | 3 | — | — | — | — | 4.71 | 3 | 4.71 | 3 | 4.71 | <1 |
| 4.08 | 2 | 220 | 4.07 | 4 | 4.08 | <1 | — | — | — | — | — | — | 4.08 | 1 | — | — | — | — | 4.08 | 1 | 4.09 | <1 |
| 3.091 | 3 | 321 | 3.081 | 1 | — | — | 3.089 | 1 | 3.103 | 1 | — | — | 3.010 | 1 | — | — | — | — | — | — | — | — |
| 2.893 | 35 | 400 | 2.898 | 27 | 2.886 | 99 | 2.900 | 31 | 2.898 | 19 | 2.886 | 58 | 2.886 | 26 | 2.891 | 30 | 2.898 | 33 | 2.898 | 46 | 2.893 | 45 |
| 2.586 | 100 | 420 | 2.590 | 100 | 2.581 | 100 | 2.591 | 100 | 2.590 | 100 | 2.586 | 100 | 2.577 | 100 | 2.585 | 100 | 2.592 | 100 | 2.592 | 100 | 2.593 | 100 |
| 2.467 | 4 | 332 | 2.472 | 16 | 2.463 | 1 | 2.471 | 11 | 2.466 | 9 | 2.466 | 11 | 2.462 | 16 | 2.466 | 9 | 2.474 | 11 | 2.471 | 7 | 2.466 | 9 |
| 2.361 | 25 | 422 | 2.362 | 27 | 2.357 | 2 | 2.367 | 24 | 2.366 | 16 | 2.363 | 21 | 2.357 | 42 | 2.360 | 13 | 2.366 | 16 | 2.366 | 21 | 2.365 | 13 |
| 2.268 | 12 | 431 | 2.269 | 19 | 2.264 | 13 | 2.276 | 17 | 2.274 | 13 | 2.264 | 18 | 2.263 | 20 | 2.268 | 15 | 2.276 | 13 | 2.270 | 12 | 2.277 | 13 |
| 2.112 | 16 | 521 | 2.120 | 22 | 2.106 | 25 | 2.118 | 13 | 2.116 | 19 | 2.109 | 10 | 2.109 | 20 | 2.113 | 11 | 2.116 | 18 | 2.116 | 14 | 2.115 | 10 |
| 2.045 | 4 | 440 | 2.051 | 8 | 2.037 | 3 | 2.053 | 5 | 2.047 | 1 | 2.046 | 10 | — | — | 2.046 | 6 | 2.043 | <1 | 2.046 | 5 | 2.046 | <1 |
| 1.876 | 20 | 611 | 1.877 | 40 | 1.874 | 28 | 1.880 | 27 | 1.882 | 13 | 1.876 | 26 | 1.874 | 36 | 1.876 | 24 | 1.881 | 16 | 1.879 | 22 | 1.878 | 11 |
| 1.828 | 1 | 620 | — | — | — | — | 1.831 | <1 | 1.831 | <1 | — | — | — | — | — | — | — | — | — | — | 1.831 | 1 |
| 1.705 | <1 | 631 | — | — | — | — | — | — | 1.706 | <1 | — | — | — | — | — | — | — | — | — | — | — | — |
| 1.669 | 10 | 444 | 1.672 | 14 | 1.668 | 29 | 1.675 | 6 | 1.675 | 9 | 1.671 | 10 | 1.668 | 26 | 1.669 | 21 | 1.675 | 14 | 1.671 | 12 | 1.672 | 11 |
| 1.604 | 30 | 640 | 1.606 | 23 | 1.603 | 40 | 1.605 | 76 | 1.607 | 26 | 1.605 | 26 | 1.602 | 58 | 1.604 | 22 | 1.609 | 29 | 1.604 | 28 | 1.608 | 49 |
| 1.574 | 2 | 552 | — | — | 1.576 | <1 | — | — | 1.573 | <1 | 1.575 | 2 | — | — | — | — | — | — | — | — | — | — |
| 1.546 | 30 | 642 | — | — | — | — | 1.551 | 43 | 1.549 | 28 | 1.543 | 44 | 1.543 | 35 | 1.546 | 26 | 1.549 | 51 | 1.550 | 47 | 1.551 | 29 |
| 1.469 | 1 | 651 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | 1.468 | 1 | — | — | — | — |
| 1.445 | 14 | 800 | — | — | — | — | 1.446 | 25 | 1.448 | 5 | 1.444 | 20 | 1.446 | 8 | 1.445 | 10 | 1.451 | 5 | 1.444 | 13 | 1.451 | 3 |
| 1.423 | 1 | 741 | — | — | — | — | 1.423 | 1 | — | — | 1.425 | 1 | — | — | — | — | — | — | 1.423 | 1 | — | — |

Table 3. *Values of the oxide ratio (FeO+MgO)/(CaO+MnO), mean radius of the X- and Y-cations (r{X} and r{Y},respectively), unit cell parameter a, cell volume V and density D of studied garnets from the Zhulti Chal and Ustrem Formations*

Таблица 3. *Стойности на оксидното отношение (FeO+MgO)/(CaO+MnO), среден радиус на X-и Y-катионите (r{X} и r{Y}, съответно), параметър на елементарна клетка a, обем на елементарна клетка V и плътност D на изследваните гранати от Жълтичалска и Устремска свити*

| Formation | No | $X_{Ca}$ (Å) | $X_{Mg}$ (Å) | r{X} (Å) | r{Y} (Å) | (FeO+MgO) / (CaO+MnO) | *a* (Å) | *V* (Å$^3$) | D (g/cm$^3$) |
|---|---|---|---|---|---|---|---|---|---|
| Zhulti Chal | 2 | 0.105 | 0.080 | 0.946 | 0.537 | 4.12 | 11.561 (4) | 1545 | 4.119 |
| | 4 | 0.042 | 0.058 | 0.933 | 0.538 | 5.63 | 11.546 (7) | 1539 | 4.181 |
| | 5 | 0.149 | 0.050 | 0.950 | 0.540 | 5.25 | 11.578 (4) | 1552 | 4.124 |
| | 6 | 0.165 | 0.053 | 0.955 | 0.540 | 3.52 | 11.597 (3) | 1559 | 4.109 |
| | 8 | 0.086 | 0.140 | 0.935 | 0.538 | 6.37 | 11.558 (3) | 1544 | 4.059 |
| | 14 | 0.053 | 0.083 | 0.931 | 0.539 | 7.28 | 11.544 (4) | 1538 | 4.172 |
| Ustrem | 9 | 0.098 | 0.104 | 0.939 | 0.538 | 5.64 | 11.552 (3) | 1541 | 4.052 |
| | 11b | 0.139 | 0.095 | 0.947 | 0.538 | 5.28 | 11.581 (3) | 1553 | 3.995 |
| | 12 | 0.145 | 0.081 | 0.948 | 0.539 | 5.30 | 11.575 (3) | 1550 | 4.020 |
| | 13 | 0.140 | 0.080 | 0.947 | 0.538 | 5.62 | 11.583 (3) | 1554 | 4.002 |

In order to compare the crystal chemical features and to clarify better the geological conditions of the garnet formation, the values of the unit cell parameter, cell volumes and densities of samples from both metamorphic formations are calculated (Table 3). As seen from Table 3 the values of *a* of the garnets from the Zhulti Chal Formation range from 11.544(4) to 11.597(3) Å while those from the Ustrem Formation – from 11.552(3) to 11.583(3) Å. The value of *a* increases more rapidly with increasing of the mean radius of the cations in octahedral (X-cations) than with increasing of the mean radius of the cations in hexahedral (Y-cations) coordination. The mean radiuses are calculated using the effective radii of Shannon and Prewit (1969), Shannon (1976). In natural garnets as a rule, increase in $X_{Ca}$ along with decrease of $X_{Mg}$ leads to increase in the value of *a* (Deer et al., 1992). Dependence between the values of *a* and $X_{Mg}$ was not observed. In all studied samples, except sample No 12, increase in $X_{Ca}$ leads to increase in the value of *a*. The unit-cell parameter of the garnet depends on isomorphic admixtures in its structure. In light of this further detailed investigations in this direction for sample No 12 are necessary.

The calculated densities of garnets from the Zhulti Chal Formation give range from 4.059 to 4.172 g/cm$^3$ and those from the Ustrem Formation – from 3.995 to 4.052 g/cm$^3$.

On the basis of the ICP AES analyses the studied garnets represent a solid solution in the almandine – grossular – pyrope – spessartine quaternary system (see Table 4). All they are almandine-rich with varying amounts of the other end members. A larger variation was observed in the molar percentages of the end members of the samples from the Zhulti Chal Formation than those of Ustrem Formation. For samples from Zhulti Chal Formation the molar percentage of almandine ranges from 70.2 to 79.0, of grossular – from 4.2 to 16.5, of pyrope – from 5.0 to 14.0 and of spessartine – from 3.6

Table 4. *ICP AES data for garnets from Zhulti Chal and Ustrem Formations.* $X_{Mg} = Mg / (Fe^{2+} + Mg + Mn + Ca)$, $X_{Ca} = Ca / (Fe^{2+} + Mg + Mn + Ca)$

Таблица 4. *ICP AES данни на гранати от Жълтичалска и Устремска свити.* $X_{Mg} = Mg / (Fe^{2+} + Mg + Mn + Ca)$, $X_{Ca} = Ca / (Fe^{2+} + Mg + Mn + Ca)$

| | Zhulti Chal Formation | | | | | | Ustrem Formation | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Oxide wt.% | 2 | 4 | 5 | 6 | 8 | 14 | 9 | 11b | 12 | 13 |
| $SiO_2$ | 36.46 | 35.61 | 33.84 | 33.75 | 35.65 | 33.77 | 37.16 | 39.35 | 38.64 | 39.32 |
| $TiO_2$ | 0.47 | 0.72 | 1.14 | 1.25 | 0.67 | 0.87 | 0.75 | 0.60 | 0.80 | 0.76 |
| $Al_2O_3$ | 19.87 | 19.72 | 20.01 | 20.18 | 20.59 | 20.59 | 20.42 | 18.76 | 18.67 | 18.57 |
| $Fe_2O_3$ | 32.78 | 35.85 | 36.32 | 33.82 | 33.31 | 37.18 | 32.93 | 32.27 | 33.24 | 33.41 |
| MnO | 4.22 | 4.61 | 1.50 | 3.41 | 2.41 | 3.12 | 2.57 | 1.55 | 1.42 | 1.27 |
| MgO | 1.86 | 1.34 | 1.20 | 1.28 | 3.28 | 1.97 | 2.35 | 2.12 | 1.85 | 1.81 |
| CaO | 3.39 | 1.36 | 4.95 | 5.59 | 2.81 | 1.75 | 3.10 | 4.35 | 4.57 | 4.40 |
| $Na_2O$ | 0.06 | 0.04 | 0.04 | 0.05 | 0.63 | 0.05 | 0.05 | 0.04 | 0.05 | 0.03 |
| $K_2O$ | 0.14 | 0.06 | 0.06 | 0.05 | 0.09 | 0.04 | 0.09 | 0.16 | 0.10 | 0.12 |
| Total | 99.25 | 99.31 | 99.06 | 99.38 | 99.44 | 99.34 | 99.42 | 99.20 | 99.34 | 99.69 |
| Numbers of ions on the basis of 12 oxygens | | | | | | | | | | |
| Si | 3.048 | 3.018 | 2.890 | 2.865 | 2.963 | 2.879 | 3.066 | 3.227 | 3.188 | 3.224 |
| Al | 0.000 | 0.000 | 0.110 | 0.135 | 0.037 | 0.121 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ti | 0.030 | 0.046 | 0.073 | 0.080 | 0.042 | 0.056 | 0.047 | 0.037 | 0.050 | 0.047 |
| Al | 1.958 | 1.970 | 2.014 | 2.019 | 2.017 | 2.069 | 1.986 | 1.813 | 1.815 | 1.795 |
| $Fe^{2+}$ | 2.062 | 2.286 | 2.333 | 2.160 | 2.083 | 2.385 | 2.044 | 1.991 | 2.063 | 2.061 |
| Mn | 0.299 | 0.331 | 0.108 | 0.245 | 0.170 | 0.225 | 0.180 | 0.108 | 0.099 | 0.088 |
| Mg | 0.232 | 0.169 | 0.153 | 0.162 | 0.406 | 0.250 | 0.289 | 0.259 | 0.228 | 0.221 |
| Ca | 0.304 | 0.123 | 0.453 | 0.508 | 0.250 | 0.160 | 0.274 | 0.382 | 0.404 | 0.387 |
| Na | 0.010 | 0.007 | 0.007 | 0.008 | 0.102 | 0.008 | 0.008 | 0.006 | 0.008 | 0.005 |
| K | 0.015 | 0.006 | 0.007 | 0.005 | 0.010 | 0.004 | 0.009 | 0.017 | 0.011 | 0.013 |
| Sum. | 7.956 | 7.957 | 8.037 | 8.053 | 8.042 | 8.037 | 7.903 | 7.841 | 7.865 | 7.840 |
| End members: | | | | | | | | | | |
| Alm | 71.20 | 78.57 | 76.57 | 70.23 | 71.60 | 78.96 | 73.35 | 72.67 | 73.85 | 74.76 |
| Grs | 10.48 | 4.24 | 14.86 | 16.53 | 8.60 | 5.29 | 9.83 | 13.95 | 14.46 | 14.02 |
| Prp | 8.00 | 5.82 | 5.01 | 5.27 | 13.97 | 8.29 | 10.37 | 9.46 | 8.14 | 8.03 |
| Sps | 10.32 | 11.37 | 3.56 | 7.97 | 5.83 | 7.46 | 6.44 | 3.93 | 3.55 | 3.20 |
| $X_{Mg}$ | 0.08 | 0.06 | 0.05 | 0.05 | 0.14 | 0.08 | 0.10 | 0.10 | 0.08 | 0.08 |
| $X_{Ca}$ | 0.11 | 0.04 | 0.15 | 0.17 | 0.09 | 0.05 | 0.10 | 0.14 | 0.15 | 0.14 |

to 11.4. For the samples from Ustrem Formation the molar percentage of almandine range from 72.7 to 74.8, of grossular – from 9.8 to 14.5, of pyrope – from 8.0 to 10.4 and of spessartine – from 3.2 to 6.4. The quantitative presence of the end members of the studied garnets from Ustrem Formation can be summarized as follows: Alm > Grs ⋚ Prp > Sps. No dependence between the quantitative presence of grossular, pyrope and spessartine end members was observed in the samples from Zhulti Chal Formation. A larger variance in the chemical composition of the studied garnets from the metamorphic rocks of Zhulti Chal Formation in comparison with those of Ustrem Formation is indicative for the larger variation in the whole-rock chemistry of the host rocks and their protoliths.

The variations in garnet compositions, particulary their MnO content, were for a long time used as an estimator of regional metamorphic grade. Miyashiro (1953) suggested that the larger $Mn^{2+}$ ions were readily incorporated in the garnet structure at lower pressure, whereas at higher pressure the smaller $Fe^{2+}$ and $Mg^{2+}$ were preferential. Thus, it was proposed that a decrease of MnO in garnet indicates an increase in grade of the regional metamorphism. Sturt (1962) demonstrated what appeared to be a general inverse relationship between (MnO + CaO) content of garnet and overall grade of metamorphism, a scheme, which was taken up and reinforced by Nandi (1967). Not all investigators, however, agreed with this. Kretz (1959) demonstrated the possible influence of coexisting minerals on the composition of other minerals. Variation in garnet composition was seen to depend not only on *P-T* variation but also on changes in the composition of the different components within its matrix as these correspond to change of metamorphic grade (Deer et al., 1997).

For Ca-poor garnets in regional metamorphic rocks the increase of the (FeO+MgO)/(CaO+MnO) ratio is indicator for rise in metamorphic grade, accompanied by decrease in the unit cell parameter of garnet. This ratio is also related to variations in pressure (Deer et al., 1997). As seen from Table 3, garnets from the metamorphic rocks of Ustrem Formation are characterized with similar oxide ratio, which is indicative for their formation in close *P-T* conditions of metamorphism. The garnets from the Zhulti Chal Formation differ from those from the Ustrem Formation by large variation in their oxide ratio. Narrow intervals in the oxide ratios variances and in the values of the unit cell parameters of the samples from Zhulti Chal Formation are indicative for weak differences in *P-T* of metamorphism in the regions of the villages of Orlov Dol, Hlyabovo and Dervischka Mogila.

Using ICP AES analyses the following trace elements were determined in the studied garnets from Zhulti Chal Formation: $P_2O_5$ (0.03-0.19 wt.%), $SO_3$ (<0.03-0.37 wt.%), Ba (10-92 ppm), Co (<10-18 ppm), Cr (63-128 ppm), Ni (<10-40 ppm), Sr (17-36 ppm), V (56-115 ppm), Zn (108-218 ppm), Zr (15-31 ppm). The values of the trace elements contents in garnets from Ustrem Formation are in more narrow ranges: $P_2O_5$ (0.07-0.20 wt.%), $SO_3$ (<0.03-0.28 wt.%), Ba (13-15 ppm), Co (<10-18 ppm), Cr (81-102 ppm), Ni (<10-27 ppm), Sr (6-19 ppm), V (59-113 ppm), Zn (104-179 ppm), Zr (16-30 ppm).

An experimental work on substitution of various elements (Be, Mg, Ca, Sr, Ba, Pb, Cu, Ni, Co, $Fe^{2+}$, Se, Y, Zn, Cd) for Mn in spessartine structure as well as replacement of Al by Sc, Y, Zr, Ti, Cr, $Fe^{3+}$ shows that Ba, Co, Ni, and Zn substituted spessartines could not be obtained and that only minor Pb could be incorporated (Hřichová, 1970). Direct refinement of the occupancy of the Z site in the structure indicates that the mechanism of F substitution in garnet is similar to the OH substitution in hydrogarnet (Smyth et al., 1990).

Of special interest is the contents of $P_2O_5$ from 0.03 up to 0.20 wt.%, which have been established in the samples on study. As seen from Table 5, the phosphorus content in garnets does not correspond to the phosphorus content in the host rocks. The weight percentages of $P_2O_5$ in host rocks of samples No 2, 9, 11b is identical, but $P_2O_5$ in garnet No 11b is one of the lowest, in contrast to that in garnet No 9, which is one of the highest. Samples № 12 from the region of village Planinovo (0.20 wt.%) and № 9 from the region of village Oreschnik (0.19 wt.%) are with largest $P_2O_5$ content among the investigated garnets. Contents in garnet of amounts from 500 to 1000 ppm of $P_2O_5$ have been proposed as a pressure indicator. Microprobe analyses performed on garnets from Dora Mraria, Western Alps show Mg + Si = Na + P substitution (Brunet, Miletich, 2000) in the garnet structure. Brunet et al. (2006) have synthesized the ultra-high pressure end-member, $Na_3Al_2(PO_4)_3$, in the 15-17 GPa range at temperatures between $1200^0$ and $1600^0$C, thus showing that the P-content in garnets can be used as a potential pressure indicator where garnet coexists with phosphate minerals.

Table 5. *The $P_2O_5$ content (wt. %) in garnets and their host rocks from the Zhulti Chal and Ustrem Formations*

Таблица 5. *Съдържание на $P_2O_5$ (wt. %) в граната и във вместващите скали от Жълтичалска и Устремска свити*

| | Zhulti Chal Formation | | | | | | Ustrem Formation | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 4 | 5 | 6 | 8 | 14 | 9 | 11b | 12 | 13 |
| Garnets | 0.08 | 0.11 | 0.17 | 0.03 | 0.12 | 0.15 | 0.19 | 0.07 | 0.20 | 0.18 |
| Host rocks | 0.12 | 0.15 | 0.22 | 0.04 | 0.07 | 0.20 | 0.12 | 0.12 | 0.13 | 0.13 |

With electron probe microanalysis it is possible to detect compositional variations even within mineral grains including garnet, where often it was found that traversing from cores to rims of grains the MnO and CaO contents decreased with a concomitant increase in FeO and MgO. Hollister (1966) concluded that this zoning arises by partitioning of MnO in accordance with the Rayleigh fractionation model between garnet and its matrix as the former grows. He drew attention to preservation of such zones, which remained unaffected by diffusion, and hence unequilibrated, throughout the later stages of the metamorphism that was presumed to have induced their growth. Concurrently, Atherton and Edmunds (1966) suggested that the zoning patterns reflect changing garnet-matrix equilibrium conditions during growth and/or polyphase metamorphism, but that once garnet is formed its zones behave as closed system unaffected by changes in conditions at the periphery of the growing grain.

Tracy et al. (1976) noted that garnets from metamorphosed pelitic assemblages show, in different metamorphic zones, element distribution patterns that are complex function of rock bulk composition, specific continuous reactions in garnet, *P-T* history of the rock, homogeneous diffusion rates in garnet, and possibly the availability of metamorphic fluids at the various stages of garnet development.

Compositional (growth) zoning in garnets from Zhulti Chal and Ustrem Formations from the frame of the Sakar pluton was studied by spot microprobe analyses along a profile line from core to the rim. The representative microprobe analyses of rim and core are listed in Table 6. Figure 4 displays Fe-Mg-Mn ternary diagrams, showing trends in the growth-zoned garnets from the rocks of Zhulti Chal and Ustrem Formations. An important advantage of such type of diagrams is that they may be used for elucidation of reactions of garnet formation, as well as of changes in the reactant assemblage.

As seen in Figure 4, sample No 2 shows a complex growth zoning. At the beginning of its growth the normal type of compositional zoning is observed and shows the increase in FeO and MgO and decrease in MnO in core-rim direction. The normal type of zoning is of prograde genesis and well documented for minerals, which were grown during increasing the temperature (Avchenko, 1982). Then the zoning trend is kinked to the reverse direction. The MnO content increases from core to the rim, along with decrease in FeO and MgO thus demonstrating the reverse type of zoning. The last is of retrograde genesis. It is a typical feature of the minerals, which were grown during decreasing the temperature. As is seen in Figure 4 the zoning path of the garnet No 2 is kinked once again and the reverse type of zoning is changed to the normal type of zoning.

The examination of the growth zoning features of sample No 2 allows suggesting garnet formation in tree different reactions, caused by a two-step change in the conditions of metamorphism. The complex compositional zoning is usually observed in garnets, which have been formed under polymetamorphic conditions. Other possible hypotheses of its genesis are the metasomatic (not applicable for

Table 6. *Representative microprobe analyses of core and rim of garnets from Zhulti Chal and Ustrem Formations*

Таблица 6. *Представителни микросондови анализи от ядрото и периферията на гранати от Жълтичалска и Устремска свити*

| | Zhulti Chal Formation | | | | | | | | | | | | Ustrem Formation | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxide | 2 | | 4 | | 5 | | 6 | | 8 | | 14 | | 9 | | 11a | | 11b | |
| wt% | core | rim | core | rim | core | rim | core | rim | core | rim | core | rim | core | rim | core | rim | core | rim |
| $SiO_2$ | 36.83 | 36.59 | 36.82 | 37.82 | 37.52 | 37.19 | 37.31 | 37.70 | 38.49 | 35.69 | 43.01 | 42.53 | 36.01 | 36.41 | 35.84 | 35.34 | 36.86 | 36.50 |
| $TiO_2$ | 0.00 | 0.05 | 0.00 | 0.05 | 0.05 | 0.00 | 0.05 | 0.05 | 0.00 | 0.06 | 0.12 | 0.00 | 0.04 | 0.04 | 0.04 | 0.04 | 0.10 | 0.07 |
| $Al_2O_3$ | 19.50 | 19.58 | 20.46 | 20.01 | 20.22 | 20.28 | 21.34 | 21.32 | 18.00 | 20.16 | 19.56 | 19.69 | 19.95 | 20.34 | 20.13 | 21.09 | 20.29 | 23.03 |
| FeO | 31.51 | 34.61 | 26.77 | 37.60 | 30.04 | 37.77 | 21.26 | 35.55 | 35.92 | 40.65 | 28.8 | 33.24 | 33.86 | 35.25 | 32.78 | 33.73 | 31.45 | 33.03 |
| MnO | 4.34 | 4.89 | 9.79 | 2.45 | 2.36 | 0.13 | 12.24 | 2.02 | 1.74 | 0.19 | 5.01 | 1.03 | 3.52 | 0.53 | 2.51 | 2.10 | 5.71 | 1.97 |
| MgO | 1.95 | 2.44 | 0.95 | 1.78 | 1.19 | 1.93 | 0.73 | 1.87 | 2.20 | 3.99 | 1.49 | 2.91 | 2.81 | 3.59 | 1.84 | 3.15 | 1.57 | 1.92 |
| CaO | 6.11 | 3.20 | 3.35 | 1.52 | 7.08 | 3.45 | 6.27 | 3.76 | 3.91 | 1.28 | 2.52 | 0.73 | 3.50 | 3.48 | 6.99 | 5.30 | 6.43 | 4.26 |
| $Na_2O$ | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 | 0.16 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 |
| $K_2O$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.60 | 0.02 | 0.00 | 0.03 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.01 | 0.01 | 0.00 |
| Total | 100.2 | 101.4 | 98.3 | 101.2 | 99.1 | 100.8 | 99.2 | 102.4 | 100.3 | 102.2 | 100.5 | 100.1 | 99.7 | 99.7 | 100.1 | 100.8 | 102.51 | 100.8 |
| Numbers of ions on the basis of 12 oxygens | | | | | | | | | | | | | | | | | | |
| Si | 2.994 | 2.966 | 3.034 | 3.048 | 3.048 | 3.005 | 3.018 | 2.985 | 3.126 | 2.879 | 3.351 | 3.321 | 2.948 | 2.955 | 2.924 | 2.858 | 2.945 | 2.910 |
| Al | 0.006 | 0.034 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.015 | 0.000 | 0.121 | 0.000 | 0.000 | 0.052 | 0.045 | 0.076 | 0.142 | 0.055 | 0.090 |
| Ti | 0.000 | 0.003 | 0.000 | 0.003 | 0.003 | 0.000 | 0.003 | 0.003 | 0.000 | 0.004 | 0.007 | 0.000 | 0.002 | 0.002 | 0.002 | 0.002 | 0.006 | 0.004 |
| Al | 1.868 | 1.871 | 1.987 | 1.901 | 1.936 | 1.931 | 2.034 | 1.989 | 1.723 | 1.917 | 1.796 | 1.812 | 1.925 | 1.945 | 1.935 | 2.010 | 1.855 | 2.074 |
| $Fe^{2+}$ | 2.142 | 2.346 | 1.845 | 2.534 | 2.041 | 2.551 | 1.438 | 2.354 | 2.439 | 2.742 | 1.876 | 2.171 | 2.318 | 2.392 | 2.236 | 2.281 | 2.101 | 2.202 |
| Mn | 0.299 | 0.336 | 0.683 | 0.167 | 0.162 | 0.009 | 0.838 | 0.135 | 0.120 | 0.013 | 0.331 | 0.068 | 0.244 | 0.036 | 0.173 | 0.144 | 0.386 | 0.133 |
| Mg | 0.236 | 0.295 | 0.117 | 0.214 | 0.144 | 0.232 | 0.088 | 0.221 | 0.266 | 0.480 | 0.173 | 0.339 | 0.343 | 0.434 | 0.224 | 0.380 | 0.187 | 0.228 |
| Ca | 0.532 | 0.278 | 0.296 | 0.131 | 0.616 | 0.299 | 0.543 | 0.319 | 0.340 | 0.111 | 0.210 | 0.061 | 0.307 | 0.303 | 0.611 | 0.459 | 0.550 | 0.364 |
| Na | 0.000 | 0.000 | 0.021 | 0.000 | 0.000 | 0.000 | 0.000 | 0.020 | 0.000 | 0.025 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.014 | 0.000 |
| K | 0.000 | 0.000 | 0.000 | 0.000 | 0.062 | 0.002 | 0.000 | 0.003 | 0.000 | 0.002 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 | 0.001 | 0.001 | 0.000 |
| Sum | 8.072 | 8.095 | 7.983 | 7.998 | 8.012 | 8.030 | 7.962 | 8.029 | 8.013 | 8.172 | 7.744 | 7.772 | 8.087 | 8.071 | 8.106 | 8.135 | 8.101 | 8.004 |
| End members: | | | | | | | | | | | | | | | | | | |
| Alm | 66.74 | 72.09 | 62.74 | 83.18 | 68.88 | 82.53 | 49.45 | 77.71 | 77.09 | 81.96 | 72.44 | 82.26 | 72.17 | 75.57 | 68.93 | 69.89 | 65.15 | 75.23 |
| Grs | 16.58 | 8.54 | 10.06 | 4.31 | 20.79 | 9.62 | 18.69 | 10.53 | 10.75 | 3.31 | 8.12 | 2.32 | 9.56 | 9.56 | 18.83 | 14.07 | 17.07 | 12.43 |
| Prp | 7.36 | 9.06 | 3.97 | 7.02 | 4.86 | 7.51 | 3.03 | 7.29 | 8.41 | 14.34 | 6.68 | 12.84 | 10.68 | 13.72 | 6.90 | 11.64 | 5.80 | 7.80 |
| Sps | 9.31 | 10.32 | 23.24 | 5.49 | 5.47 | 0.34 | 28.84 | 4.47 | 3.78 | 0.39 | 12.76 | 2.58 | 7.60 | 1.15 | 5.35 | 4.41 | 11.98 | 4.54 |

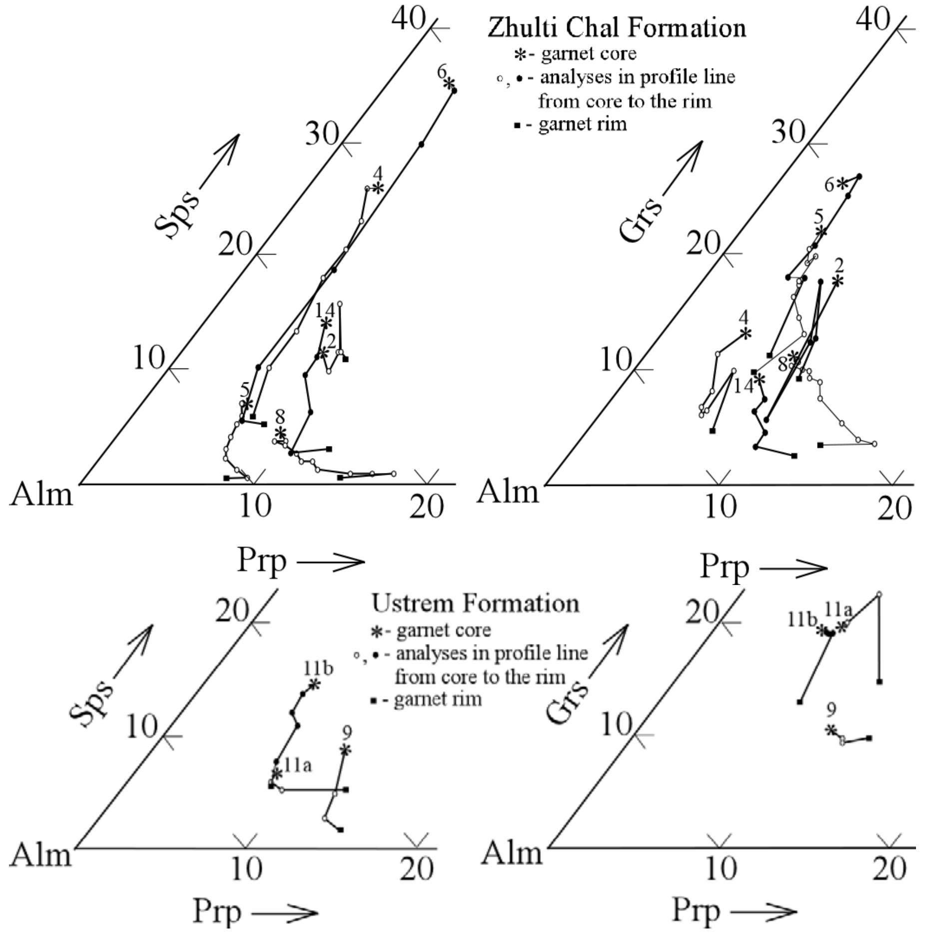


Fig. 4. Almandine-pyrope-spessartine and almandine-pyrope-grossular (in mol.%) ternary plots, showing zoning paths of garnets from Zhulti Chal and Ustrem Formations. The numbers of the samples are marked near their core analyses

Фиг. 4. Трикомпонентни диаграми алмандин-пироп-спесартин и алмандин-пироп-гросулар (в молни проценти), показващи особеностите в химичната зоналност на гранати от Жълтичалска и Устремска свити. Номерът на образците е обозначен в близост до анализите на техните ядра

garnets with size up to 2 mm, in case of sample No 2) and monometamorphic ones. The last explains formation of complex type of zoning in one metamorphic cycle, by involving new minerals in the garnet forming reaction (it is not applicable for "pelitic" chemical composition of the rocks and absence in them of other Ca-bearing minerals, except plagioclase and garnet) (Avchenko, 1982).

The zoning trend of sample No 4 shows a constant content of MnO at the beginning of its growth. Then the garnet growth was under conditions of a continuous increase of the temperature thus forming a normal type of compositional zoning. Most probably, the smooth and continuous zoning path of sample

No 4 corresponds to growth during a single reaction.

Samples No 6 and No 14 show similar trends in their growth zoning. Taking into account this fact, as well as the similarity in the mineral composition of their host rocks, it is reasonable to assume that both crystals were formed due to one and the same reaction. Mg-rise in the rims of both samples is recorded. The zoning trend of sample No 14 shows decrease in MnO in its rim, which is a retrograde growth feature in the end of its formation.

Samples No 5 and No 8 are characterized by normal type of growth zoning. Fe-increase 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 edge accompanied by formation of a more magnesian phase such as chlorite or biotite would drive the garnet compositions in direction like this (Tracy, 1982).

The zoning trends of garnets No 9 and No 11b from the rocks of Ustrem Formation are similar to that of garnet No 6 from Zhulti Chal Formation. At the beginning of its growth sample No 11a from amphibolites from Ustrem Formation shows a normal type of growth zoning. Then the trend of its zoning path was drived into direction of MnO increase from core to the rim. It is possible this change in MnO component to be caused by change in garnet forming reaction in relation to spessartine end member.

The content of CaO in garnets with normal and reversed type zoning may change in different way. For the normal type of zoning CaO content usually decreases from core to rim direction in the crystal. The change in the Ca component to a great extent correlates with this of Mn component in the studied samples, except garnet No 11b. In this sample the calcium component is nearly constant and only in the rim decrease in its value was observed (Fig. 4). The Ca zoning in garnet may be influenced by other minerals present in the host rock, which are richer in Ca like epidote, plagioclase, and apatite. It can be assumed that the increase of Ca content in the rims of some garnets results from incorporation of a calcium-containing phase such as plagioclase and epidote in the garnet forming reaction.

The change in the trend of Ca zoning in sample No 9 could be explained with the so-called diffusion zoning, which differs from the growth zoning by being imposed over already grown crystals. The diffusion zoning realizes in conditions of intercrystalline diffusion, which results from reaction between the garnet crystal surface and adjacent mineral. It can develop during heating or cooling of the rocks and can be a source of data about the progress of the mineral reactions and also about the retrograde processes. In the mineral assemblage of garnet in sample No 9, which displays a normal type of zoning, there is plagioclase whose basicity increases towards the periphery (anorthite in the core is 16.5 wt.%, whereas in the rim it is 20.8 wt.%). As the content of CaO in this garnet lowers from core to the rim it can be supposed that there is a redistribution of CaO between garnet and plagioclase, caused by changes in *P* and *T* conditions. It is to be noted that the effect of redistribution of cations between minerals can not be explained with simple metasomatic acts (at nearly constant *P* and *T*). As metasomatism is characterized by directed import-export of components this must lead to concordant increase or decrease of the weight percentage of these components in all Ca-bearing minerals in the association. In other words, the ratios Ca/(Ca + Fe + Mg + Mn) in garnet and Ca/(Ca + Na) in plagioclase must concordantly increase or decrease in conditions of metasomatism at nearly constant *P* and *T*. According to Avchenko (1982) in all quartz-containing assemblages without $Al_2SiO_5$ the temperature increase or pressure decrease leads to redistribution of CaO from garnet to plagioclase and the reverse effect is determined by lowering of *T* or increase of *P*.

All discussed above determines that

garnet is an important petrogenetic indicator and main descriptor of the thermodynamic conditions.

## Conclusions

1. All studied garnets are almandine rich with varying amounts of the other end members.
2. The crystal chemical characteristics of almandines from the metamorphic rocks of the Zhulti Chal Formation, suggest larger variations in the chemical composition of the host rocks and their protoliths respectively, as well as larger variations in the physical conditions of the metamorphism (temperature and pressure) of these rocks in comparison with those of the Ustrem Formation.
3. Polymetamorphic conditions of the garnet growth (garnet formed in tree different reactions, caused by two-step change in the physical conditions of the metamorphism) are suggested only for sample No 2 from the region of the Orlov Dol village. All other studied garnets show growth under conditions of continuous increase of temperature thus forming a normal type of compositional zoning. In their zoning paths retrograde growth features were recorded only in their rims.
4. The change in the calcium component in garnets to a great extent correlates with this of manganese, with exception of sample No 9 from the region of Oreschnik for which diffusion zoning is suggested.

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