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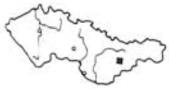
COMPOSITIONAL ZONING OF GARNETS FROM THE VEPORIDE CRYSTALLINE ROCKS

(Tab. 1, Pls. 4, Figs. 15)



Abstract: Garnets from the veporide rock samples were studied in detail by making electron microprobe analyses. Compositional zoning and compositional variations of garnet end-members were determined. The compositional zoning is primarily due to irregular and mainly marginal position of grossular component. The almandine — grossular zones of garnet originated as a result of the retrograde metamorphism, and/or the consequence of metasomatic reactions associated with Ca — mobilization.

Резюме: Автор при исследовании гранатов из образцов веноридных пород при помощи электронового микроанализатора определили их зональный состав и изменения в замещении отдельных месторождениях граната. Зональность гранатов вызвана главным образом неравномерным и также краевым положением гроссулярового компонента. Возникновение альмандино-гроссуляревых зон граната считается результатом процесса ретроградного метаморфоза, или последствием метасоматических реакций, соединенных с Са — мобилизацией.

Introduction

Analyses of garnets from 17 samples of the veporide crystalline were made on an electron microprobe analyser. The compositional zoning and variations of garnet end-member molecules were determined in 4 samples.

The type and the degree of compositional zoning may be a characteristic one for some rock groups and individual rocks with certain mineral associations. Compositional zoning of garnets reflects non-equilibrium conditions between the grain and the host rock during the growth or during the successive development of the rock and it may be caused by:

a) metamorphic grade (A. Miyashiro, 1953; R. St. J. Lambert, 1959; S. Banno, 1965; B. W. Evans, 1966; G. Kurat — H. G. Scharbert, (1972),

b) metamorphic grade and influence of Rayleigh fractionation principle (L. S. Hollister, 1966; B. Harte — K. J. Henley, 1966; B. E. Leake, 1967; E. Fediuková, 1973),

c) metamorphic grade, fractionation and differentiation in diffusion velocities (B. Harte — K. J. Henley, 1966; M. L. Crawford, 1966; B. E. Leake, 1967; E. Fediuková, 1973; J. Olimpio — D. E. Anderson, 1978).

Experimental

The "method of heavy fractions from ground rocks" introduced by M. Žabka — J. Veselský (1976) was applied. The JEOL JXA — 5A electron

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Table 1

Chemical analyses of garnets (wt. %)

Sample	V—9_1	V—9_2	V—21_1	V—21_2	V—17_1	V—17_2	V—41_1	V—41_2
SiO_2	34,86	34,84	34,79	33,87	33,96	33,70	32,92	32,97
Al_2O_3	22,63	21,86	22,56	22,05	23,11	22,37	20,68	21,91
FeO	35,53	30,88	31,80	28,02	35,60	33,89	36,88	29,20
MnO	2,59	3,22	7,90	7,18	2,96	0,20	3,67	3,15
MgO	3,00	0,62	3,41	0,61	4,46	1,26	2,15	0,97
CaO	2,59	11,60	1,47	10,93	1,28	4,46	1,69	11,14
Σ	101,20	103,00	101,93	102,96	99,66	97,60	97,00	99,34
Cation contents based on 12 oxygens								
Si	2,81	2,78	2,79	2,73	2,76	2,81	2,74	2,72
Al	2,14	2,05	2,13	2,09	2,21	2,20	2,09	2,13
Fe^{2+}	2,39	2,06	2,13	1,88	2,30	2,48	2,64	2,01
Mn	0,17	0,22	0,53	0,49	0,20	0,01	0,26	0,22
Mg	0,36	0,07	0,40	0,07	0,57	0,15	0,27	0,12
Ca	0,22	0,99	0,12	0,94	0,11	0,39	0,15	0,98
Garnet end-members (mole %)								
Alman.	75,83	61,59	66,53	55,57	72,88	81,32	79,09	60,30
Pyrop	11,44	2,20	12,74	2,15	17,10	5,11	8,23	3,59
Spess.	5,62	6,51	16,76	14,46	6,46	0,48	7,99	6,60
Gross.	7,10	22,69	3,95	27,80	3,54	13,07	4,67	29,50

microanalyzer was used to establish homogeneity of chemical composition by means of main elements X-ray images and line profiles. The quantitative analyses of main components were carried out using pure Fe, Mn, Mg, Al and wollastonite (for Ca and Si) as standards. Accelerating voltage 20 kV, beam current 3×10^{-7} A, raw data were reduced applying the ZAF correction procedures (computer program SONDA 03).

For garnet end-member calculations total Fe was considered as Fe^{2+}. The theoretical approach to establish number of Fe^{3+} cations, as proposed by H. Szimazaki (1977), when $Al + Fe^{3+} = 2$ (on the basis of 12 oxygens), was not relevant because of the Al^{3+} exceeding the limit of 2. Consequently, the total number of Ca atoms was employed to calculate grossular molecule proportions.

Chemical composition of zonal garnets

Chemical analyses of garnets, cation contents based on 12 oxygens and molecule fractions of garnet end-members are listed in Table 1. Labelling of samples (index 1, 2, e. g. V-9_1, V-9_2) represents two quantitative analyses of garnet grain from one and the same sample.

Petrographic description of samples under consideration can be found in the works of M. Mudráková (1978) and E. Krist (1973, 1979). The localization of samples follows like this:

Migmatized biotite paragneiss, sample V-9, locality: Kamenistá dolina valley, 250 m NW of elev. p. 732, 4.

Migmatized biotite paragneiss, sample V-21, locality: quarrier in the road cut, 500 m S of Utekáč.

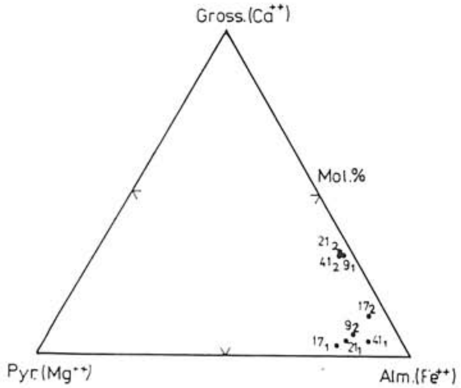


Fig. 1. Plot of analyzed garnets on a pyrope — grossular — almandine diagram.

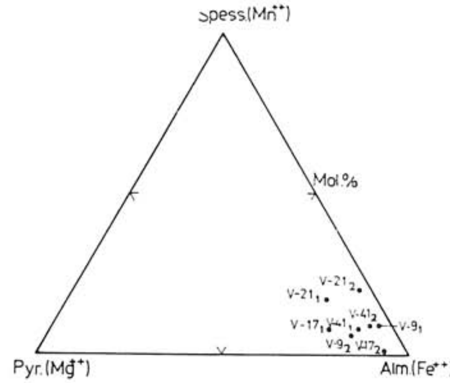


Fig. 2. Plot of analyzed garnets on a pyrope — spessartite — almandine diagram.

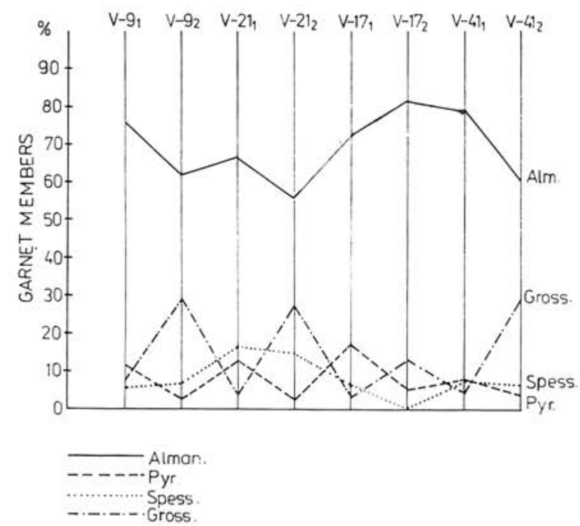


Fig. 3. Variations of end-members in studied garnets.

Diaphthorite of migmatites of mica schist character, sample V-41, locality: Podtajchová dolina valley, 50 m downwards of elev. p. 643,4. Exposure in the forest path cut, ranging to approximately 200 m.

Mylonitized biotite granitoide with porphyroblasts of pink feldspars — the "Vepor" type, sample V-17, locality: Rimavice dolina valley, 300 m SW of the elev. p. 768,4.

The distribution of analyzed zonal garnets in the part of the triangle pyrope — grossular — almandine (Fig. 1) and pyrope — spessartite — almandine (Fig. 2) manifests the evident miscibility of almandine, grossular (Fig. 1) and in a lower degree also the pyrope and spessartite components (Fig. 2).

The light zones (designated index 1), in comparison with the dark zones (designated index 2), exhibit increased content of almandine — pyrope and spessartite components (sample V-9 is an exception to this) while the grossular component decreases (Fig. 3). The tie lines of the individual point analyses

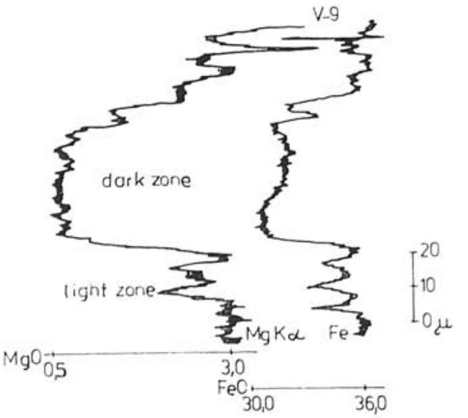


Fig. 4. Mg Kα and Fe Kα line profiles of zonal garnets, sample V-9.

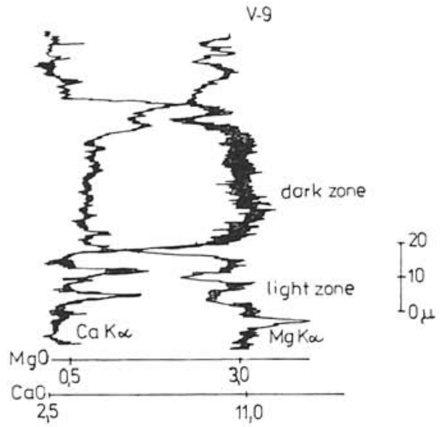


Fig. 5. Mg Kα and Ca Kα line profiles of zonal garnets, sample V-9.

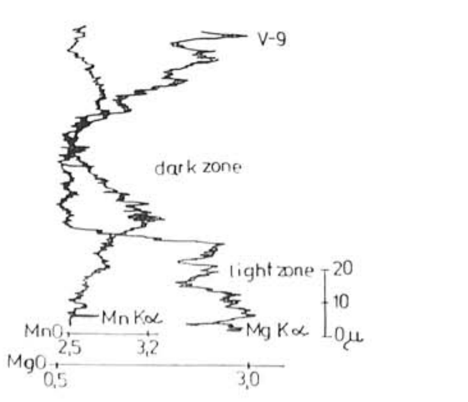


Fig. 6. Mn Kα and Mg Kα line profiles of zonal garnets, sample V-9.

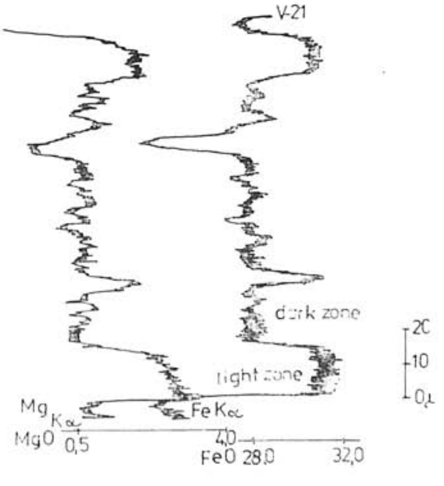


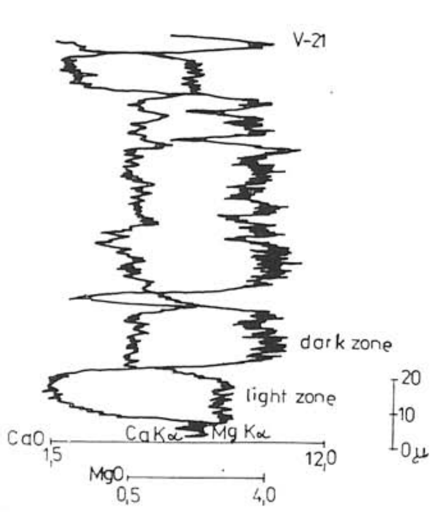
Fig. 7. Fe Kα and Mg Kα line profiles of zonal garnets, sample V-21.

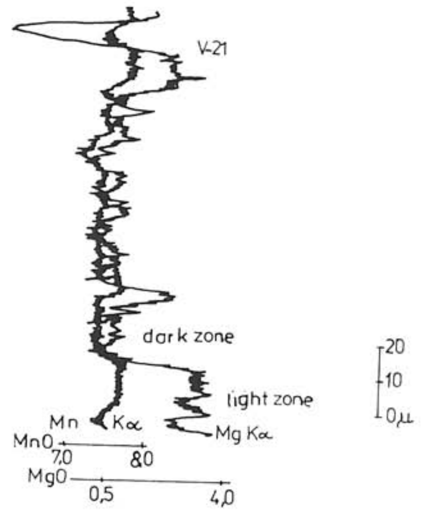
do not represent gradual changes of chemical composition within analyzed garnets, they are meant to emphasize graphically differences of garnet component contents within one single crystal and mutually between the individual samples.

Distribution of elements in zonal garnets

The essential works (M. P. Atherton — W. D. Edmunds, 1966; F. Hollister, 1966; B. W. Evans, 1966; M. P. Atherton, 1968; E. H. Brown, 1969 etc.) present the view that almost all garnets are zonal in metamorphic rocks studied so far, mainly in metapelites, with Mn and Ca-rich crystal centers and with Mg and Fe-rich rims.

It is a universally accepted rule (A. Miyashiro, 1953; B. A. Sturt, 1962; K. Nandi, 1967 in P. Árkai et al., 1975) that the average FeO and MgO contents increase in garnets, the CaO and MnO contents decrease with





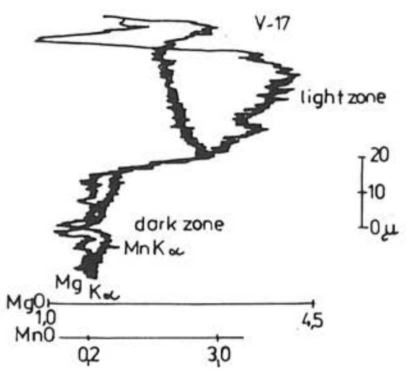


Fig. 8. Ca Kα and Mg Kα line profiles of zonal garnets, sample V-21.
Fig. 9. Mn Kα and Mg Kα line profiles of zonal garnets, sample V-21.
Fig. 10. Mg Kα and Mn Kα line profiles of zonal garnets, sample V-17.

increasing temperature and pressure throughout the progressive metamorphism. When applying this rule to compositional zoning of metamorphic garnets, MnO and CaO contents gradually decrease and FeO and MgO contents increase from the crystal center towards its edges during the progressive metamorphism. In the opposite case, the retrograde compositional zoning takes place (O. Amit, 1976).

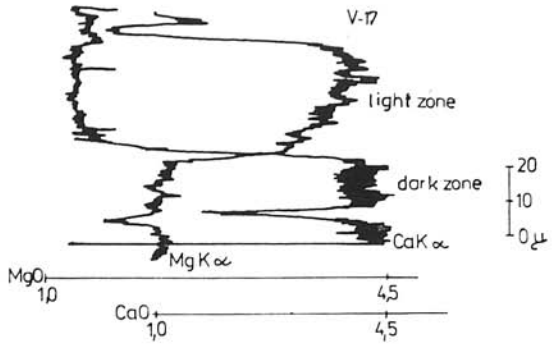


Fig. 11. Mg Kα and Ca Kα line profiles of zonal garnets, sample V-17.

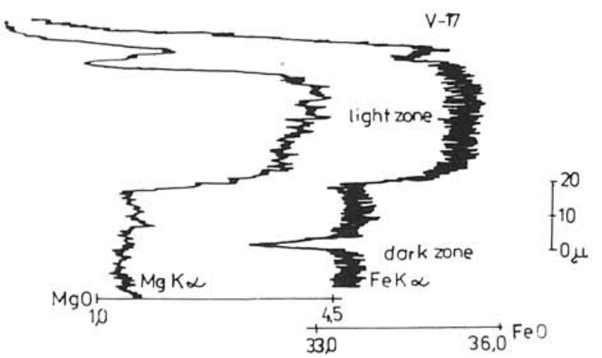


Fig. 12. Mg Kα and Fe Kα line profiles of zonal garnets, sample V-17.

E. H. Brown (1969) explains the compositional zoning of garnets mainly by the change of the environment composition in which they originated and by delimited diffusion, not by the change of pressure — temperature conditions during the crystallization. However, D. E. Anderson — G. R. Buckley (1973) consider the temperature changes in metamorphism to be an important factor, affecting also the diffusion coefficients.

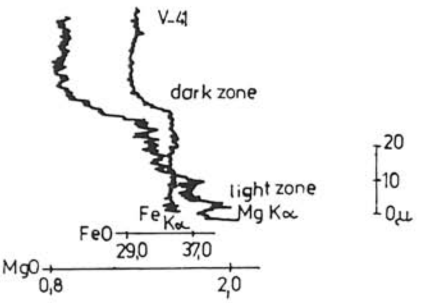
P. Árkai et al. (1975) present the following conditions to be kept (one or several) so that compositional zoning of minerals takes place:

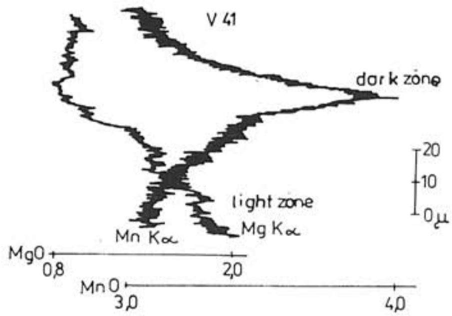
— the change of the chemical environment — its composition during the crystallization of the mineral,

— the diffusion velocity of the elements forming the zonal mineral is lower in the mineral — forming environment than the velocity of the mineral growth,

— the change of pressure — temperature conditions of the crystallization.

Distribution of elements in zonal garnets under consideration is not unambiguous. Garnets from the veporide migmatized paragneisses share the following common features of compositional zoning: (the light zone) rich in Fe, Mg,





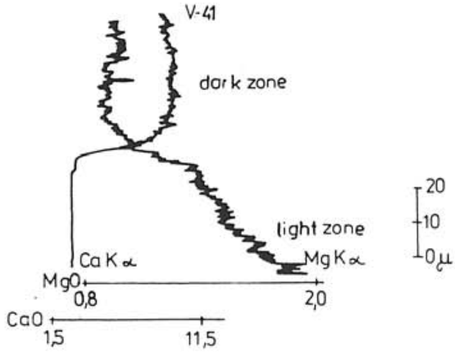


Fig. 13. Fe Kα and Mg Kα line profiles of zonal garnets, sample V-41.
Fig. 14. Mg Kα and Mn Kα line profiles of zonal garnets, sample V-41.
Fig. 15. Mg Kα and Ca Kα line profiles of zonal garnets, sample V-41.

Mn and (the dark zone) rich in Ca. An exception to this was found in garnet from sample V-9, where the Mn content in the dark zone is higher by approximately 1 %. The Mn content in light and dark zones in the mentioned sample varies within the range 1—2 %.

Another variation was found in garnet from sample V-17, where (the light zone) is enriched in MnO — 2.96 % and it decreases to 0.20 % in the dark zone.

According to A. Miyshiro (1953), R. St. J. Lambert (1959), the MnO content in garnets decreases with the temperature increase. B. Harte — K. J. Henley (1966), M. P. Atherton (1968) as well as K. Nandi (1967) in P. Árkai et al. (1975) stated that higher MnO content in garnets of pelitic schists is the consequence of the growth at lower metamorphic grade. It is explained by gradual loss of MnO in the rock system during the crystallization of garnet. It follows from the mentioned facts that the changes of the element composition in garnet are in close relation with their contents in the host rock and with the crystallization of other minerals. P. Béthune — P. Goosses — P. Berger (1965) suggested that the decrease of Mn content in garnet

Plate I.

Compositional zonal garnet, sample V-9. Magn. 300x.

a — Composition and Ca Kα, Mg Kα and Fe Kα line profiles, b — Composition and Si Kα, Al Kα and Mn Kα line profiles, c — Ca Kα X-ray image, d — Fe Kα X-ray image, e — Mg Kα X-ray image, f — Mn Kα X-ray image.

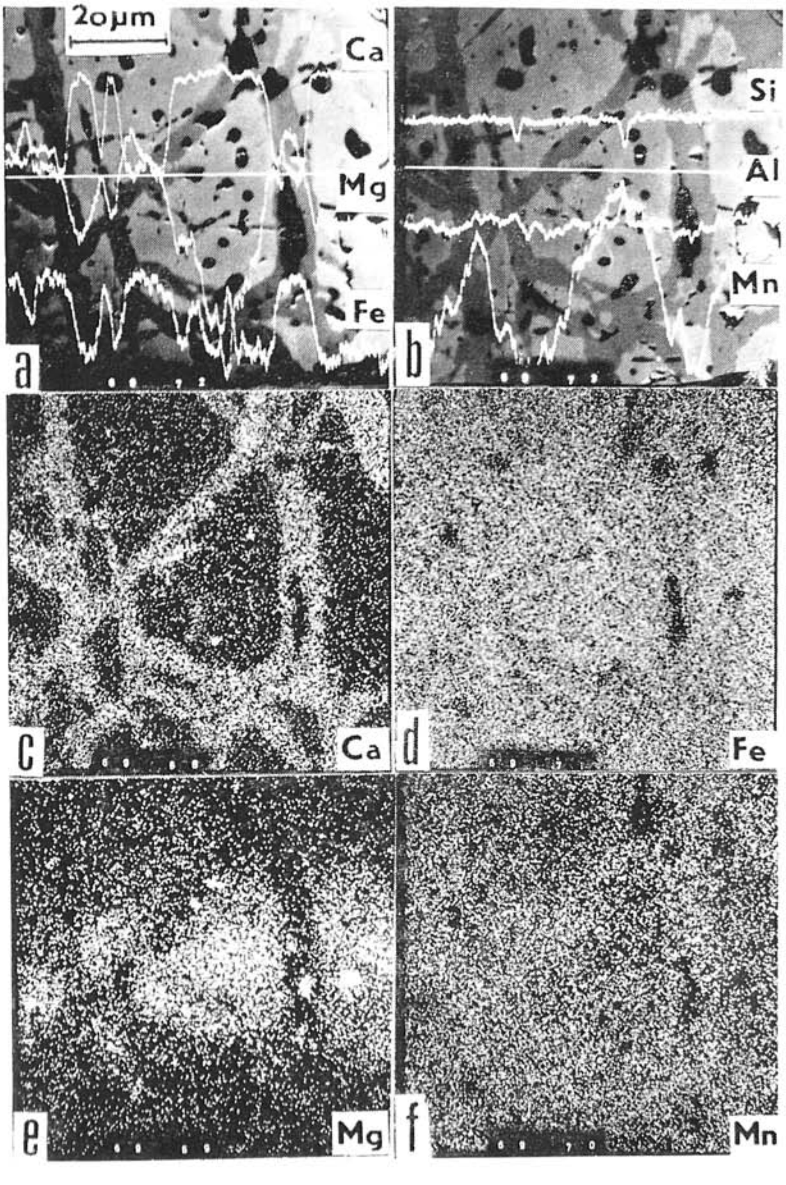


Plate II

Compositional zonal garnet, sample V-21.

a — Compositional and Mn $K\alpha$, Ca $K\alpha$ and Fe $K\alpha$ line profiles, magn. 300x, b — Composition and Al $K\alpha$, Si $K\alpha$ and Mg $K\alpha$ line profiles, magn. 300x, c — Si $K\alpha$ X-ray image, magn. 600x, d — Al $K\alpha$ X-ray image, magn. 600x, e — Ca $K\alpha$ X-ray image, magn. 600x, f — Fe $K\alpha$ X-ray image, magn. 600x.

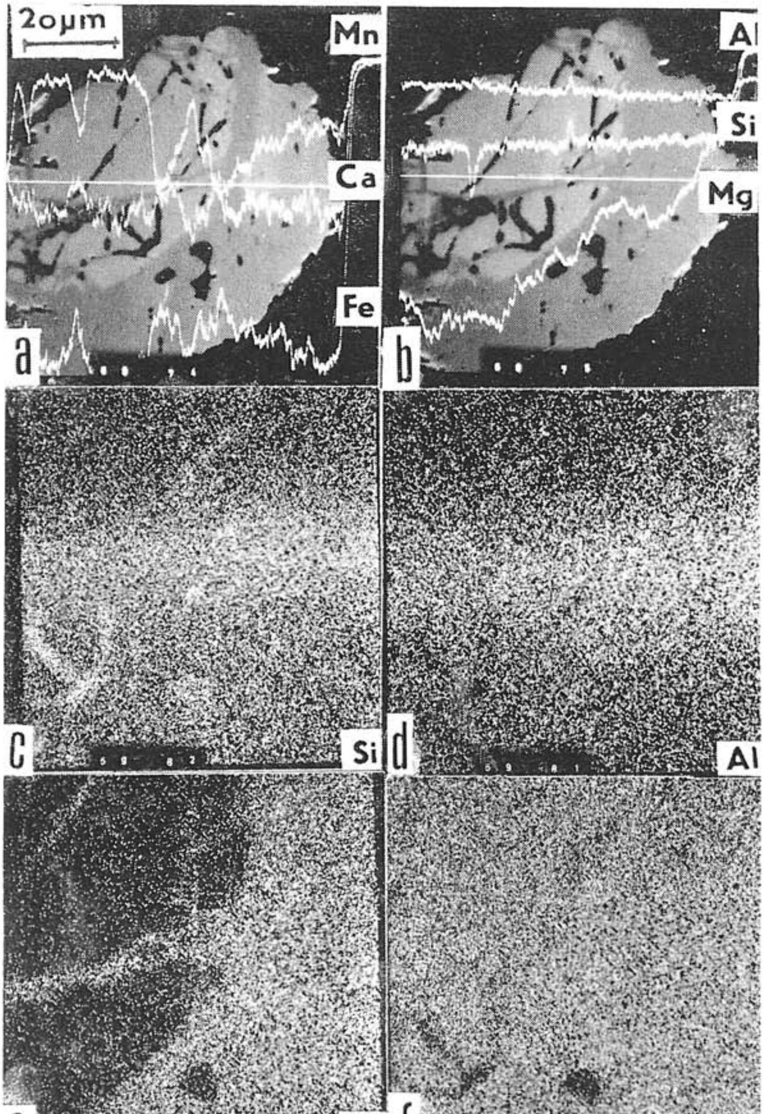


Plate III

Compositional zonal garnets, samples V-21, V-17.

a— Mn Kα X-ray image, magn. 600x, sample V-21, b — Mg Kα X-ray image, magn. 600x, sample V-21, c — Composition and Ca Kα and Fe Kα line profiles, sample V-21, d — Composition and Mn Kα and Mg Kα line profiles, magn. 300x, sample V-21, e — Another example of zonal garnet composition, magn. 300x, sample V-21, f — Composition of zonal garnet, magn. 300x, sample V-17.

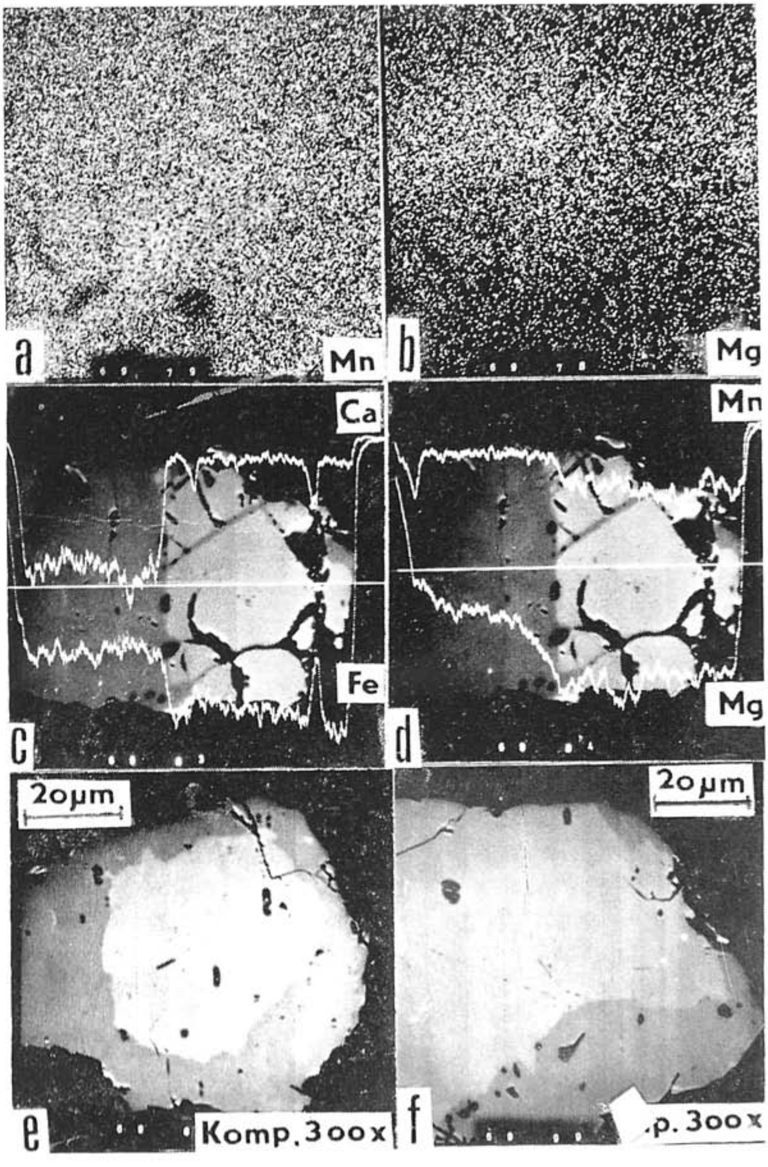
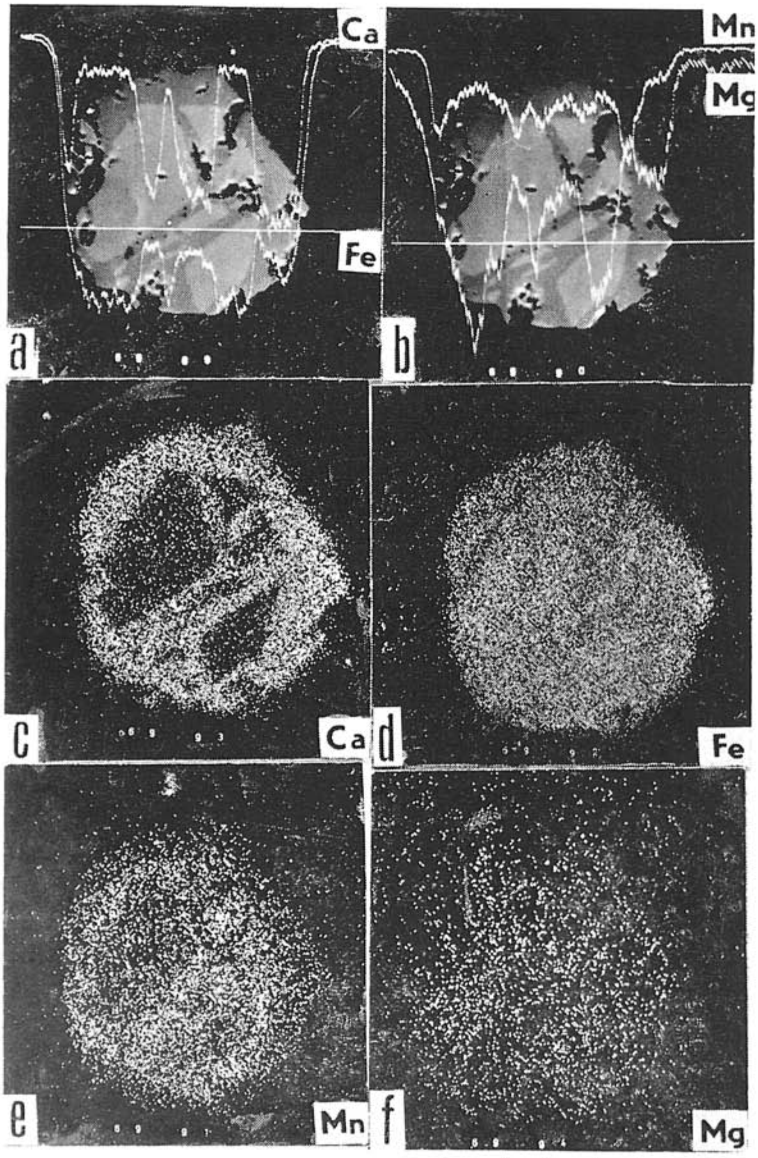


Plate IV

Compositional zonal garnet, sample V-41, magn. 300x.

a— Composition and Ca $K\alpha$ and Fe $K\alpha$ line profiles, b — Composition and Mn $K\alpha$ and Mg $K\alpha$ line profiles, c — Ca $K\alpha$ X-ray image, d — Fe $K\alpha$ X-ray image, e — Mn $K\alpha$ X-ray image, f — Mg $K\alpha$ X-ray image.



from the center to the edges of the grain is closely associated with the mechanism processes of progressive metamorphism: in their view, the central part of garnet is the part of the crystal which originated in chlorite and biotite metamorphic zone in which the highest Mn content in the rock concentrates. After the change of thermodynamic conditions, when the rock, due to progressive metamorphism, passed into the almandine zone, garnet grew up to the edges with decreased or zero Mn content and increased Fe content. From the mentioned facts it follows that the light zone of garnet in sample V-17 originated at lower metamorphic grade and by the change of thermodynamic conditions, toward the higher metamorphic grade, the formation of dark zone took place. The process can be explained by metasomatism and/or retrograde metamorphism of originally metamorphic garnet (regarding low MnO content). Therefore, garnet in granitoide may be of metamorphic origin, i. e. it represents the relic of paracrystalline in the rock.

G. Kurat — H. G. Scharbert (1972) and E. Fediuková (1973) also assume that the Mn content in garnets of moldanubicum rocks decreases with temperature increase from the center towards the edges and the Fe content increases.

G. Müller and A. Schneider (1971) re-investigated the changes of garnet chemical compositions in metapelites from the Stavanger area — Norway, which hav been already described by V. M. Goldschmidt (1922). According to their results, the MnO content in garnets decreases in dependence on decrease of temperature. It can be seen, that the changes of garnets with decrease of temperature show the similar trend in all baric types. The MnO content decreases and the FeO content increases. The MgO content increases with further increase of temperature.

Conclusions

On the basis of the investigation results, it can be assumed that the compositional zoning of garnets under consideration originated during the retrograde metamorphic process, by filling the cracks of originally disintegrated progressive metamorphic garnets. Disintegration of garnet grains was preceded by progressive metamorphism.

This compositional zoning can be characterized by increased Ca content, while decrease of Fe, Mg and partly Mn can be observed.

Compositional zoning of this type may be explained by the entry of free Ca into the garnet structure. The free Ca is the product of retrograde metamorphic reactions (amphibole $\longrightarrow$ biotite, garnet $\longrightarrow$ biotite $\longrightarrow$ andesine $\longrightarrow$ oligoclase $\longrightarrow$ albite) characterized by high P_{H_2O} and low P_{CO_2}, which took place in marginal zone of migmatite granitization. Another reason for that phenomenon is the Ca-metasomatism of "basic front" connected with migmatization (P. Árkai et al., 1975).

The kind of Fe, Mn, Mg and Ca partitition in the individual garnet zones from the veporide crystalline rocks can be regarded as prove of distinct growth phases. They reflect outstanding and probably unified phases of the metamorphic history of the rock. They provide a helpful tool in determining the relation of garnet formation with its further development.

Compositional zoning of garnets can be explained by applying several factors (metamorphic grade, fractionation, differentiation of diffusion velocities), while the diffusion factor took place later on as follows from line profile analyses.

Substantial differences in chemical composition of dark zone and the light zone of the garnet were discovered. The type of compositional zoning is practically identical in all samples under consideration. The dark zones of garnets are Ca-rich and the light ones are rich in iron, magnesium and manganese.

This type of compositional zoning is different from usual compositional zoning of progressively metamorphic garnets, described in literature as the "normal" one (Ca, Mn maximum in the center and Fe, Mg in the edges), which is the result of the retrograde metamorphism, and/or the consequence of the metasomatism.

Translated by H. Budajová

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