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COMPOSITIONAL ZONING IN GARNETS FROM GRANULITE FACIES ROCKS OF THE MOLDANUBIAN ZONE, BOHEMIAN MASSIF OF LOWER AUSTRIA, AUSTRIA

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Garnets from granulite facies rocks of the Moldanubian Zone of Austria have been analyzed with the electron-microprobe. All garnets were found to be compositionally zoned. Zonation patterns vary and also differ from those known from garnets in low grade metamorphic rocks. Ca and Fe always exhibit the known zonation patterns (Ca enriched in garnet center, Fe enriched at edges). Mn is generally distributed evenly in most of the garnets and, if variable, exhibits a 'reverse' zoning (enriched at edges as compared to cores). These Mn zonation patterns suggest either readjustment of garnet surface compositions to lower temperature conditions or garnet growth falling temperature. Evenly distributed elements within the central portion of garnets, the rather common even distribution of Mn throughout garnets, and the low fractionation factors for Mn between garnets and rock systems suggest a rather high-temperature origin of the Austrian Moldanubian granulites.

1. Introduction

Zonation is common in many metamorphic minerals. Since the electron-microprobe has become a widely used tool in petrological investigations, many cases of compositional zoning have been discovered. Zonary structures in garnets have been described from mesozonal pelitic schists [1–6], Norwegian eclogites [7] and eclogites from northern Spain [8]. A slightly zoned garnet from a charnockite of the Varberg area, Sweden, has also been mentioned [9].

Two kinds of zonation trends have been recognized [6]:(1) The zonary arrangement is regular, and the variation in the content of an element may be described by a single curve of a bell-shaped form. Such patterns are typical of continuous growth during one metamorphic event. (2) The zonary arrangement irregular. At least two metamorphic events are necessary for the development of such a pattern [10].

Generally in regular zonations Ca and Mn are concentrated in the core, whereas Mg and Fe show a reverse tendency. The interpretations of this type of zoning are given in [3] and [5], and we will call such purely descriptively 'normal zoning'. Both Atherton [3] and Hollister [5] explain the 'normal' Mn enrichment in the core of garnets by a Mn fractionation mechanism between the local rock system and the growing garnet. There exist, however, other interpretations involving garnet growth during increasing grade of metamorphism [2]. All these investigations have been carried out on garnets which were taken from mesozonal pelitic schists, and therefore came from a lower grade of metamorphism than the granulite facies garnets described here. Deviations from this 'normal zoning' have been reported and attributed to special growing conditions. Vogel and Bahezre [8] presented an example of 'reverse' FeO and CaO zoning from an eclogite of northern Spain. Oscillatory zoning of CaO has also been found [4], and marginal Mn-enrichment has been reported from contact metamorphic rocks [10].

In the Moldanubian Zone of the Bohemian Massif of Lower Austria, granulite facies rocks are rather significant for the interpretations of the metamorphic history of that area. The reader is referred to [12–14] for further information. These rocks belong to the "two pyroxene facies group" [11]. The marginal parts of the complexes often suffered retrograde metamorphism. Only rocks without visible retrograde mineral assemblages have been chosen for this study.

Garnet is an essential constituent in all rocks although it only exceptionally exceeds 12% by volume. Garnet crystals never develop crystallographic faces but exhibit curved surfaces. Grain shape and size vary considerably. Earlier unpublished investigations by means of X-ray diffractometer have revealed a slight split of the (640) and (642) reflections in various specimens. This feature was ascribed to a non-uniform composition of the garnet phase [cf. 1].

A total of 25 garnets from 5 different rocks were analyzed using a JEOL-JXA3 and an ARL-EMX electron-microprobe X-ray analyzer. Analyzing conditions were 15 kV acceleration potential and 0.2 or 0.15 μA sample current respectively. Analyses were performed by stepscanning across the entire grain. All elements were measured against a wet-chemically analyzed, homogeneous garnet. Corrections were made for drift, background, mass absorption, secondary fluorescence and atomic number. For the computations a modified version of the computer program written by Rucklidge [15] was used.

2. The composition of the garnets

Specimens were taken from the following granulite facies areas [13]: Dunkelstein Forest (DW 379, DW 823), Pochlarn-Wieselburg (PW 427, PW 517), both situated in the south, and Gopfritz (GOP 801) from the center of the Moldanubian Zone of Lower Austria.

Rock compositions vary widely ranging from pyroxene granulites to pyriclasites*. Table 1 shows the mod-

* Bulk-chemical compositions, mineral contents and mineral compositions have partly been published [14].

Table 1

Modal composition of granulite facies rocks considered in this paper. DW 379, DW 823, GOP 801 pyroxene granulites, PW 427 intermediate pyriclasite, PW 517 pyriclasite.

	DW 379	DW 823	GOP 801	PW 427	PW 517
Quartz	30.1	27.0	16.5	1.9	-
Alkalifeldspar	1.6	4.3	3.2	-	-
Plagioclase	46.8	45.7	56.2	67.6	5.4
Garnet	10.6	11.5	3.6	2.5	1.6
Orthopyroxene	7.4	9.5	10.3	15.4	81.2
Clinopyroxene	-	-	1.6	5.5	-
Biotite	2.5	0.6	7.3	4.3	6.1
Opaques	0.8	1.3	1.2	2.7	4.2
Accessories	0.2	0.1	0.1	0.1	0.5

Table 2

Electron-microprobe analyses of garnets from granulite facies rocks of the Moldanubian Zone, Lower Austria.

	DW 379		DW 823				GOP 801		PW 427		PW 517	
			part 1		part 2							
	R	C	R	C	R	C	R	C	R	C	R	C
SiO_2	37.4	37.2	36.5	36.3	36.4	36.7	38.1	37.8	38.0	37.6	38.7	39.5
TiO_2	0.3	0.23	0.38	0.38	0.35	0.38	0.03	0.1	0.2	0.2	0.04	0.04
Al_2O_3	19.8	20.3	20.3	20.0	20.3	20.5	21.7	19.1	21.0	20.1	22.8	23.3
FeO*	32.3	30.0	31.7	27.7	31.3	29.2	28.2	19.3	28.2	24.9	22.8	16.9
MnO	0.6	0.5	0.83	0.68	0.81	0.7	1.36	0.43	1.67	0.64	1.15	0.9
MgO	5.2	4.6	4.5	3.8	4.4	4.0	4.7	5.1	3.8	5.1	12.0	14.4
CaO	4.6	7.5	5.8	10.2	6.0	8.3	5.9	18.0	7.0	11.2	2.3	5.0
Total	100.2	100.3	100.0	99.3	99.6	99.8	100.0	99.8	99.9	99.7	99.8	100.0
Cation numbers on the basis of 12 oxygens:												
Si_{IV}	2.98	2.95	2.92	2.92	2.93	2.93	3.00	2.97	3.00	2.97	2.94	2.93
Al_{IV}	0.02	0.05	0.08	0.08	0.07	0.07	–	0.03	–	0.03	0.06	0.07
Al	1.84	1.85	1.89	1.82	1.85	1.87	2.01	1.74	1.96	1.84	1.84	1.96
Ti	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Fe	2.15	1.99	2.12	1.82	2.10	1.95	1.85	1.27	1.87	1.64	1.45	1.05
Mn	0.04	0.03	0.05	0.05	0.06	0.05	0.09	0.03	0.11	0.04	0.07	0.06
Mg	0.62	0.55	0.54	0.45	0.53	0.47	0.55	0.06	0.49	0.60	1.36	1.59
Ca	0.39	0.63	0.49	0.88	0.55	0.71	0.50	1.51	0.59	0.95	0.19	0.40
Composition in terms of end-members:												
Py	19.3	17.2	16.8	14.1	16.5	14.8	18.4	17.6	16.0	18.6	44.3	51.3
Alm	67.2	62.2	66.3	56.9	65.2	61.3	61.9	37.2	61.1	50.8	47.2	33.9
Gr	12.2	19.7	15.3	27.4	16.5	22.3	16.7	44.3	19.3	29.4	6.2	12.9
Sp	1.3	0.9	1.6	1.6	1.8	1.6	3.0	0.9	3.6	1.2	2.3	1.9

* Total Fe as FeO.

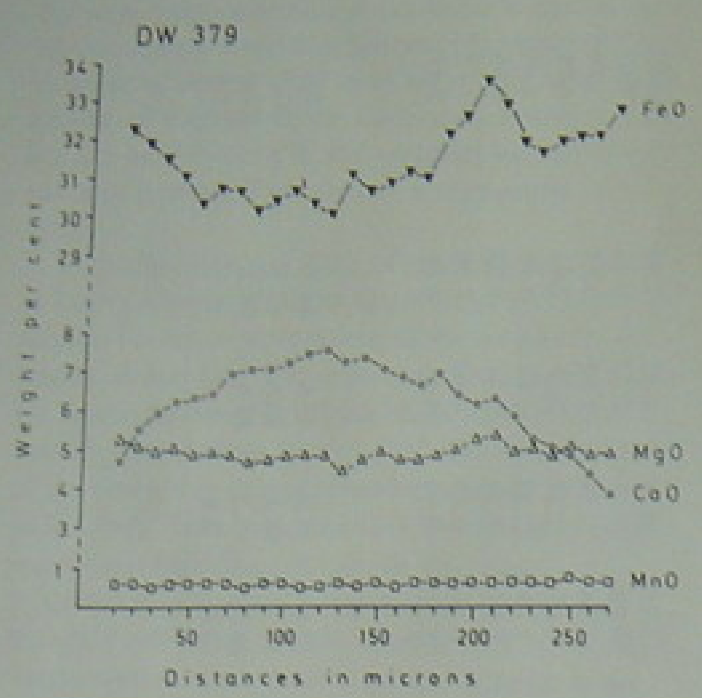

Fig. 1a.

al compositions of the selected samples. Ilmenite is the most abundant opaque phase; pyrrhotite and rarely magnetite may also be present. Common accessories are apatite, rutile and zircon.

The chemical composition of the garnets, the cations calculated on the basis of 12 oxygens, and the concentrations of end-member molecules are listed in table 2. Representative analysis for rims (*R*) and centers (*C*) of individual garnets are given. The corresponding microprobe traces are shown in fig. 1.

The garnet bulk compositions lie within the range for garnets from "charnockites and granulites" [16]. Garnets from GOP 801, however, clearly lie outside this range due to their high CaO contents. Garnets of such composition are rather rare, but have been described from glaucophane-schists [17], various types of eclogites [18] and from a charnockite of the Varberg area, Sweden [9].

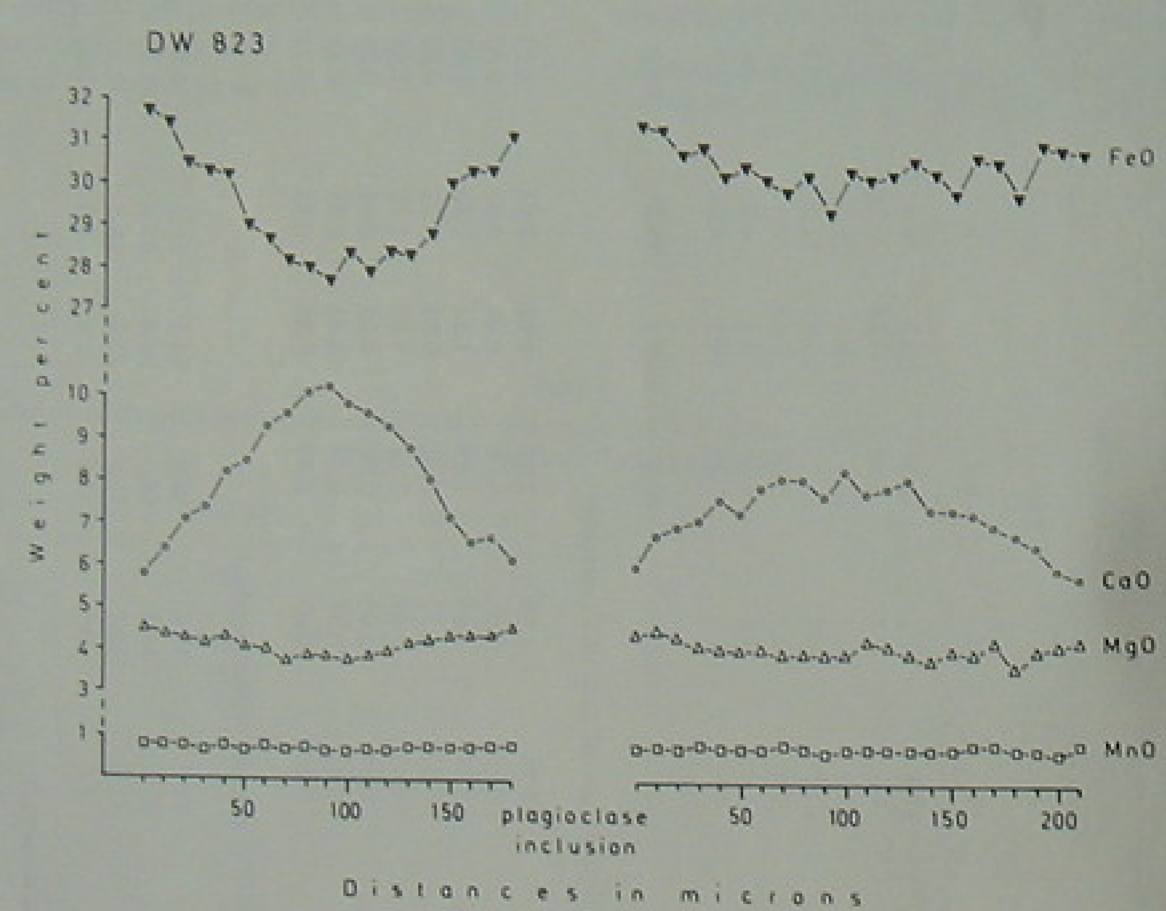

Fig 1b.

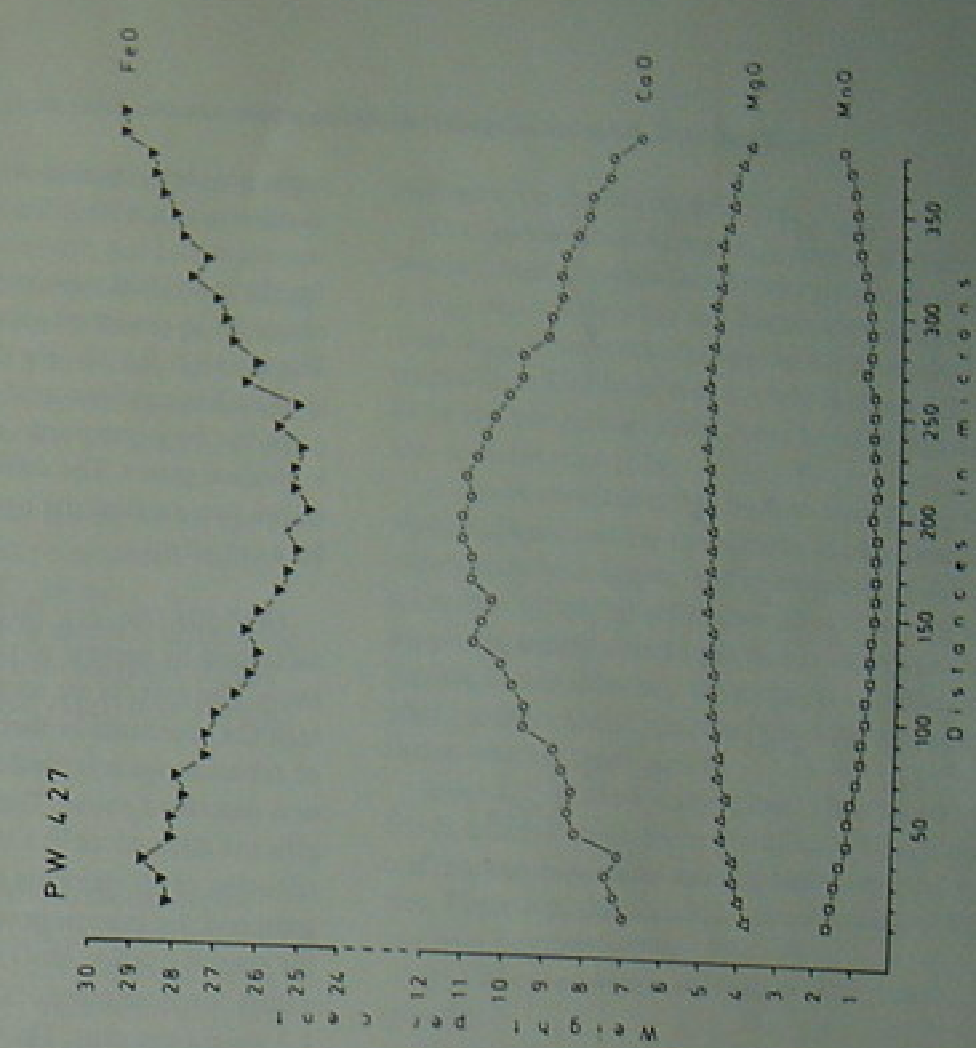

Fig. 1d.

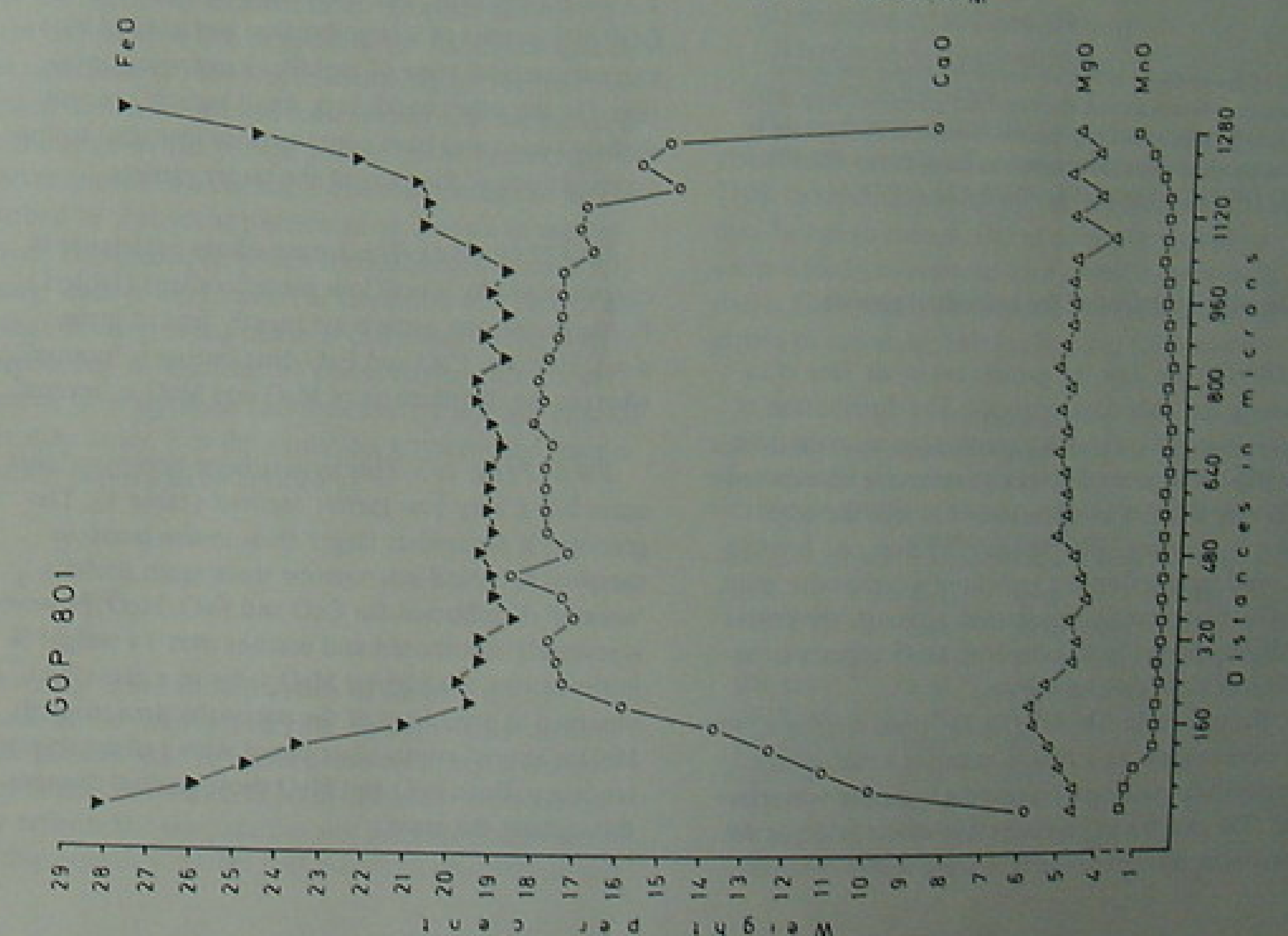

Fig. 1c.

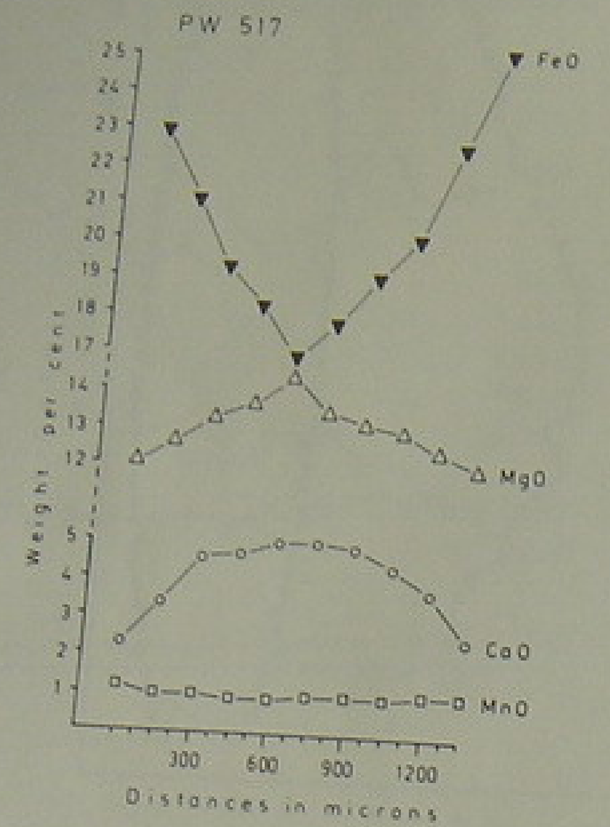

Fig. 1e.

Fig. 1. Edge-to-edge electron-microprobe step-scans across garnets in Lower Austrian Moldanubian granulite. Step intervals have been adjusted to grainsize. Compositional zoning is evident in all samples. Description in the text. (a) DW 379, (b) DW 823, (c) GOP 801, (d) PW 427, (e) PW 517.

3. Zonation patterns of the individual garnets

DW 379 (fig. 1a): the garnets are small, free of inclusions, and only slightly zoned. The distribution of CaO is 'normal' i. e., with a continuous increase from the edge to the core. FeO is also normally distributed with only a rather small increase towards the edge. There is, however, some irregularity near one boundary which may reflect the growth of a composite grain. MgO is nearly evenly distributed, although the center is slightly poorer in this element. MnO appears to be constant throughout the grain.

The garnets in *DW 823 (fig.1b)* again display a rather weak zoning. As a typical example a microprobe step scan containing a plagioclase inclusion was selected. The two traces on either side of the feldspar are somewhat different. The first trace shows the maximum possible zonation which has also been detected in other grains within the same section. The second trace reveals a less pronounced zoning. The patterns for the individual elements, however, are of the same character as described above for garnets from DW 379. The traces in fig. 1b give the impression that the plagioclase has not been enclosed by one single garnet grain but by a composite garnet consisting of several individual grains. The differences in the composition of the two parts of the probe trace can be explained by a cut effect.

GOP 801 (fig. 1c): this pyroxene granulite is characterized by garnets of variable sizes and compositions. The garnets are strongly zoned and show very high CaO contents in their cores. The general pattern of zonation again is similar to that exhibited by garnets described above. There are, however, some significant differences like the nearly homogeneous distribution of all elements in the central portion of the grain and the inhomogeneous distribution of MnO. In the central portion MnO is evenly distributed, but within the outermost 100 microns it rises from 0.6 to 1.5 weight per cent. Thus, average-sized garnets in GOP 801 consist of a large portion surrounded by a narrow marginal zone of rapidly changing composition. On the other hand, very small garnets are only slightly zoned and have compositions identical to the compositions of the rims of the larger garnets.

PW 427 (fig. 1d): This intermediate pyriclasite is characterized by a very low garnet content (table 1). Furthermore, the garnets are mostly free of inclusions. Here the CaO and FeO distribution is 'normal', whereas the distribution of MgO and MnO is 'reverse'.

PW 517 (fig. 1e): This hypersthene-rich pyriclasite again has a very low garnet content (table 1). The grainsize is somewhat larger than in the previous samples. A typical microprobe trace again shows a 'normal' distribution for CaO and FeO. MgO, however, is reversely distributed and reaches over 14 weight % in the center, the highest MgO value in a garnet yet observed in granulites of the particular area studied. MnO is almost evenly distributed with a slight reverse tendency. Both FeO and MgO show gradual changes throughout the grain.

In summary the compositional zoning in garnets from the Moldanubian granulite facies rocks of Lower Austria shows:

(1) CaO and FeO in all cases exhibit 'normal' (CaO high in centers, FeO high at edges). The degree of zoning, however, varies, and the distribution of the elements may be either continuously changing over the entire grain or change more or less abruptly near the edge of the grain.

(2) MgO usually shows a flat zoning which can be 'normal' or 'reverse'. The most pronounced zoning occurs in a garnet of high MgO content.

(3) MnO is generally very low and it is distributed evenly in most of the grains we investigated. Zoned distributions are always 'reverse' (MnO high at edge).

4. Discussion

Zonation in garnets from various metamorphic rocks has been explained by a continuous fractionation between the local rock system and the growing garnet [3, 5]. Provided that: (1) there is no diffusion of the particular element in the growing garnet; (2) the diffusion of this element in the local rock system is rapid; and (3) the fractionation factor for that element between the local rock system and the garnet is constant over the growth period of the garnet, the development of a regular elemental zoning can be described by a physical phenomenon, known as segregation. This principle, which is widely used in zone refining, leads to enrichment or depletion of a certain element in the growing phase as compared to the system depending on whether the fractionation factor k between growing phase and rock system is larger or smaller than unity. For the garnet-rock system the fractionation factor can be defined as

$$k = \frac{C_E^{\text{Garnet center}}}{C_E^{\text{rock}}},$$

where C_E is the concentration of element E [5].

Of all the elements varying regularly in metamorphic garnets, Mn has been chosen by many investigators as that one which in its distribution most probably reflects the temperature and pressure conditions during growth [19]. We will therefore concentrate our discussion on the Mn distribution.

The fractionation factors k_{Mn} found by us in Moldanubian granulite facies rocks are shown in table 3. k_{Mn} varies somewhat and lies between 3.5 and 7.7. Thus, k_{Mn} in our rocks is lower by far than those reported from Dalradian rocks, where it diminishes from 81 in the low-grade mineral zones to 28 in the staurolite–kyanite zone [5].

It can be concluded that temperatures during the Moldanubian granulite facies metamorphism must clearly have been higher than those necessary for the formation of amphibolite facies rocks. This view is supported by the observation that in some rocks the garnets do not show any Mn-zoning at all, which implies equilibration of Mn-distribution by thermal diffusion whithin those garnets.

Since k_{Mn} is above unity, garnet growth under the conditions metioned above should also reveal a 'normal' zoning, i. e., enrichment of MnO in garnet centers. Therefore, the observed 'reverse' zoning of MnO can only be explained by:

(1) falling temperature during or after garnet growth;

(2) changing crystallization rates;

(3) late mineral reactions; and

(4) changing pressure.

The changing crystallization rate was probably effective in short-lived contact metamorphic events [10]. In regional metamorphism crystallization rates may be apt to change. Dramatic changes, however, are not likely to occur in deep seated metamorphic rocks. Since we do not observe any formation of new phases in our rocks, also explanation (3) does not

Table 3

MnO contents of garnet centers and bulk chemical composition (in weight per cent) of the corresponding rocks together with the fractionation factor k_{Mn}. Bulk MnO contents from unpublished analyses.

Specimen	MnO bulk	MnO garnet center	k_{Mn}
DW 379	0.08	0.5	6.2
DW 823/I	0.09	0.68	7.5
DW 823/II	0.09	0.7	7.7
GOP 801	0.12	0.43	3.6
PW 427	0.1	0.64	6.4
PW 517	0.27	0.9	3.3

apply. Furthermore, the pressure dependence of elemental distribution coefficients has been shown to be rather weak [20]. A very strong pressure increase would be necessary to account for the change in k_{Mn}, which seems to be remote.

The only explanation applicable for the observed 'reverse' zoning of Mn is the hypothesis of falling temperature (explanation (1)). Within this model there are two possibilities:

(1) Garnet equilibrated at or near the climax of the granulite facies metamorphism. Because of the high temperatures involved, the mobility of Mn in the garnet is high enough to readjust by diffusion to the changing (falling) temperature at the garnet-rock system interface according to a changing (increasing) k_{Mn}. No recrystallization or further growth is necessary for this adjustment.

(2) Garnet nucleated at or near the climax of the granulite facies metamorphism and continued to grow with falling temperature.

Probably both cases are applicable to some of our rocks. Garnets showing an even distribution of Mn and other elements in the central portion (fig. 1c) can be the product of both growing models. No preference can be given to one of the models. One conclusion, however, can certainly be drawn from this distribution: temperatures during growth or annealing of the central portion must have been high enough to provide equilibration by diffusion. Equilibrated distribution of elements in garnets are common in eclogites [7] and high-grade metamorphic rocks [21]. This is a characteristic feature of garnets from very high temperature metamorphic environments. This view is also supported by the low k_{Mn}.

Equilibrated distributions of Mn solely are very probably the result of garnet growth or annealing at a somewhat lower temperature as compared to the eclogite environment. Although no data are available on ionic diffusion in garnets, we may conclude that Mn probably is one of the elements with the highest diffusion rates in pyralspite garnets.

All garnets, except from GOP 801, regardless whether they show an equilibrated or non-equilibrated Mn distribution, show for most of the other elements a continuously changing distribution. This feature again can be explained by both models given above. The regular and continuous change of composition in those garnets, however, is best explained by a continuous garnet growth with falling temperature.

According to the compositional characteristics of the garnets, the granulite facies rocks of the Moldanubian Zone of Lower Austria investigated by us are high-temperature metamorphic rocks. In some of the rocks the garnet probably nucleated late and growth took place partly with falling temperature after the climax of the deep-seated granulite facies metamorphism. More detailed work on the mineralogy of the granulite facies rocks of the Moldanubian Zone of the Bohemian Massif of Lower Austria is in progress.

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References

[1] S. Banno, Notes on rock-forming minerals (34). Zonal structure of pyralspite garnet in Sambagawa Schists in the Bessi Area, Sikoku, J. Geol. Soc. Japan 71 (1965) 185.
[2] B. Harte and K. J. Henley, Occurrence of compositionally zoned garnets in regionally metamorphosed rocks, Nature 210 (1966) 689.
[3] L. S. Hollister, Garnet zoning: an interpretation based on the Rayleigh fractionation model, Science 154 (1966) 1647.
[4] L. S. Hollister, Contact metamorphism in the Kwoiek Area of British Columbia: an end member of the metamorphic process, Geol. Soc. Am. Bull. 80 (1969) 2465.
[5] M. P. Atherton, The variation in garnet, biotite and chlorite composition in medium grade pelitic rocks from the Dalradian, Scotland, Contrib. Mineral. Petrol. 18 (1968) 347.
[6] M. P. Atherton and W. M. Edmunds, An electron microprobe study of some zoned garnets from metamorphic rocks, Earth Planet. Sci. Letters 1 (1966) 185.
[7] I. Bryhni and W. L. Griffin, Zoning in eclogite garnets from Nordfjord, West Norway, Contrib. Mineral. Petrol. 32 (1971) 112.

[8] D. E. Vogel and C. Bahezre, The composition of partially zoned garnet and zoisite from Cabo Ortegal, N. W. Spain, N. Jahrb. Mineral. (Mh.) (1954) 140.
[9] S. K. Saxena, Chemical study of phase equilibria in charnockites, Varberg, Sweden, Am. Mineralogist 53 (1968) 1674.
[10] W. M. Edmunds and M. P. Atherton, Polymetamorphic evolution of garnet in the Fanad aureole, Donegal, Eire, Lithos 4 (1971) 147.
M. Okrusch, Garnet–cordierite–biotite equilibria in the Steinach Aureole, Bavaria, Contrib. Mineral. Petrol. 32 (1971) 1.
[11] E. den Tex, The facies groups and facies series of metamorphism, and their relation to physical conditions in the Earth's crust, Lithos 4 (1971) 23.
[12] A. Köhler, Die moldanubischen Gesteine des Waldviertels und seiner Randgebiete, Fortschr. Mineral. 25 (1941) 153.
R. Reiss, Beiträge zur Kenntnis der Gesteine des niederösterreichischen Waldviertels, Thesis, University of Vienna.
[13] H. G. Scharbert, Die Granulite de südlichen niederösterreichischen Moldanubikums, I, N. Jahrb. Mineral. (Abh.) 100 (1963) 59.
[14] H. G. Scharbert, Die Granulite des südlichen niederösterreichischen Moldanubikums, II, III, N. Jahrb. Mineral. (Abh.) 101 (1964) 27, 210.
H. G. Scharbert, Beobachtungen am Granulitkörper von St. Leonard am Horner Wald, niederösterreichisches Waldviertel, Anz Akad. Wiss. Wien 5 (1967) 201.
H. G. Scharbert, Granulitfazies im Moldanubikum der Böhmischen Masse Niederösterreichs, Freib. Forschungsh. C 268 (1971) 81.
H. G. Scharbert, Cyanite und Silimanite in Moldanubischen Granuliten, Tschermaks Mineral. Petrol. Mitt. 16 (1971) 252.
[15] J. Rucklidge, A computer program for processing microprobe data, J. Geol. 75 (1967) 126.
[16] E. Tröger, Die Granatgruppe: Beziehungen zwischen Mineralchemismus and Gesteinart, N. Jahrb. Mineral. (Abh.) 93 (1970) 1.
[17] A. Pabst, The garnets in the glaucophane schists of California, Am. Mineralogist 16 (1931) 327.
T. W. Bloxam, Glaucophane schists and associated rocks near Valley Ford, California, Am. J. Sci. 257 (1959) 95.
I. Y. Borg, Glaucophane-schists and eclogites near Healdburg, California, Geol. Soc. Am. Bull. 67 (1956) 1563.
[18] M. J. O'Hara and E. L. P. Mercy, Exceptionally calcic pyralspite from South African kyanite eclogite, Nature 210 (1966) 68.
N. V. Sobolev, N. I. Zyuzin and I. K. Kuznetsova, The continuous pyrope-grossularite series of garnets in the grospydites, Dokl. Akad. Nauk SSSR 167 (1966).
A. M. Reid, J. Z. Frazer and H. Fujita, Garnet analysis, Scripps Inst. Oceanogr., Ref. 69–21.
N. V. Sobolev, A. I. Butkunov and I. K. Kuznetsova, A diamond-bearing eclogite with calcium-rich garnet from the 'Mir' pipe (Yakutia), Geol. i. Geofis. 4 (1959) 125.
[19] R. Kretz, Some applications of thermodynamics to coexisting minerals of variable composition. Examples: orthopyroxene–clinopyroxene and orthopyroxene-garnet, J. Geol. 69 (1961) 361.
L. P. Greenland, D. Gottfried and R. I. Tilling, Distribution of manganese between coexisting biotite and hornblende in plutonic rocks, Geochim. Cosmochim. Acta 32 (1968) 1149.
[20] H. Ramberg and G. DeVore, The distribution of Fe^{++} and Mg^{++} in coexisting livines and pyroxenes, J. Geol. 59 (1951) 193.
[21] R. W. White, Ultramafic inclusions in basaltic rocks from Hawaii, Contrib. Mineral. Petrol. 12 (1966) 245.
H. Kuno, Mafic and ultramafic nodules in the basaltic rocks of Hawaii, Geol. Soc. Am. Mem. 115 (1969) 189.
G. Kurat, Granat–Spinell–Websterit und Lherzolith aus dem Basalttuff von Kapfenstein, Steiermark, Tschermaks Mineral. Petrol. Mitt. 16 (1971) 192.