

SOME ZONED GARNETS FROM THE GREENSCHIST FACIES

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ABSTRACT

Microprobe analyses and phase relationships of zoned garnets from quartzo-feldspathic schists of several different greenschist facies terranes suggest the following interpretations of garnet paragenesis:

One likely garnet producing reaction in the greenschist facies is: chlorite+epidote+quartz→garnet+water. The calculated dP/dT for the equilibrium condition of this reaction is very large, and negative in the P - T region of the greenschist facies.

Although for most garnets the major portion of the zoning is caused by Mn-depletion, garnets in a few specimens are associated with enough phases so that they should be compositionally invariant at constant grade. Zoning in these garnets is probably caused by increase in grade. Many garnets are zoned strongly in Fe and Mn but not in Ca. According to the reaction given above this is reasonable if the Al-content of the chlorite and epidote which break down remains constant during garnet growth. Further, garnets with high grossularite content will form in rocks in which the activity of Al is relatively low with respect to that of Fe and Mn.

INTRODUCTION

A previous work by this writer (Brown, 1967, pp. 281-5) describes some zoned garnets from the greenschist facies of Otago, New Zealand. In this paper new analyses are presented of garnet and coexisting minerals from the greenschist facies of Otago, Scotland, Vermont, and the Cascades of northwest Washington. These are pertinent to the nature of garnet producing reactions, the controls of zoning paths and the relationships of garnet composition to metamorphic grade. Much has been written on these subjects and for background the reader is referred to papers by: Sturt (1962), Banno (1965), Albee (1965), Hollister (1966), Atherton (1965, 1968), Saxena (1968).

OBSERVATIONS

Chemical Analyses. All chemical analyses (Tables 1-3) were performed with an electron microprobe. The analytical technique is the same as that described in Brown (1967, p. 261-2). Because ferric and ferrous iron cannot be distinguished and H₂O cannot be determined with the probe the analyses in these respects are less satisfactory than wet chemical determinations. In a few cases the summations depart significantly from 100. This is partly due to analytical error, but for biotite and chlorite is surely also due to the presence of some Fe₂O₃ and probably also more or less H₂O than the ideal amount, which was used in the summation. For the garnets Fe, Mn, Ca were measured simultaneously and Mg, on a later run in specimens: 4-18, 4-24, 8-31, 17-4, and 668-276. Fe, Mg, Ca were run together and Mn later for garnets; 668-15, 668-63, 668-213. From analyses of aluminum on several garnets it was judged that very little andradite is present (see Brown, 1967, p. 283). The analytical error, which is largely due to inhomogeneity of garnet standards, is judged to be ± 2 percent of the amount of garnet end-member present.

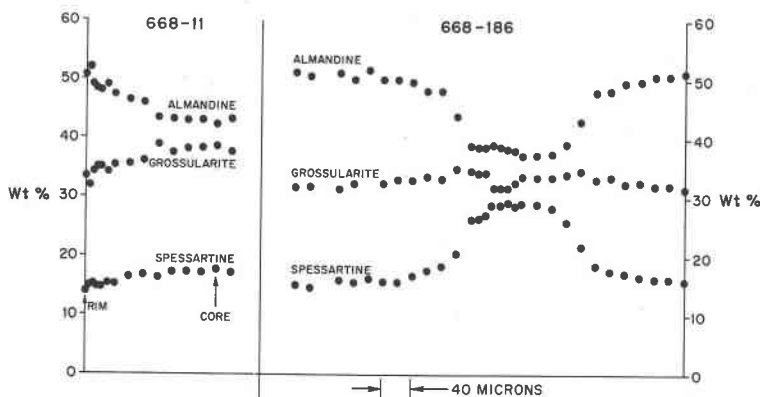


FIG. 1. Zoning profiles of two garnets from New Zealand. See Brown (1967, p. 284) for other profiles.

For each garnet grain studied some 5 to 30 spots were analysed at 5, 10, or 20 micron intervals on a traverse across the grain. One to four grains were studied in each specimen and all the grains in each specimen lie within the 2-centimeter wide field of a single polished thin-section. Profiles of the zoning are given in Figure 1 and also in Brown (1967, p. 284). The garnets, except for the rims of a few, consist almost entirely of the three end members almandine, spessartine, grossularite and thus their compositions can be well represented on a ternary diagram. In plotting the results the analysis of each spot is adjusted to 100 percent almandine+spessartine+grossularite and is represented by a point on the ternary diagram. An arrow is drawn showing the direction of zoning from core to rim (Fig. 2).

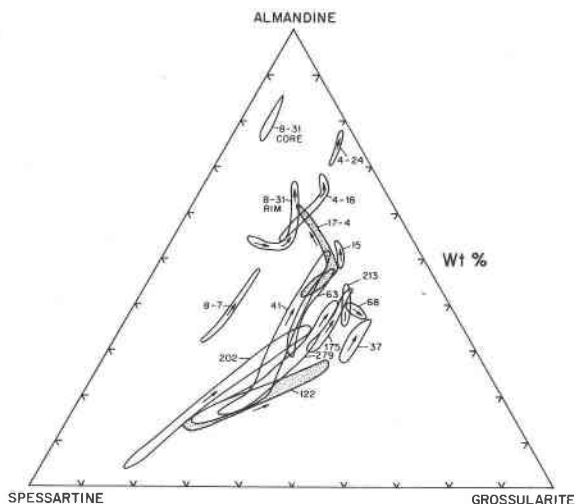


FIG. 2. Plot of the composition of analysed points on garnet in 668-11. Analyses have been normalized to the components of the diagram. The arrow points in the direction of zoning from core to rim.

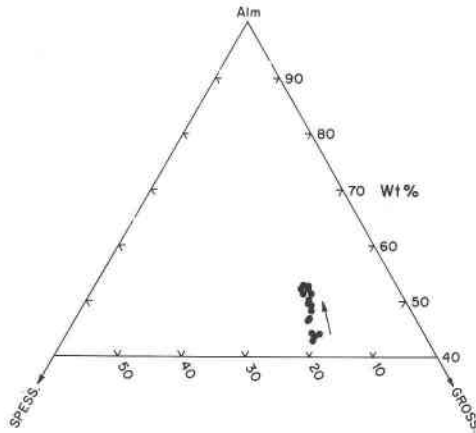


FIG. 3. Zoning paths of garnets. The area shown for each specimen is based on from 10 to 30 analysed points (see text and Fig. 1), generally the larger the area the more points are available. Pyrope makes up less than 2 wt% of all compositions except those on the rims of 4-18, 4-24, 8-31, and 17-4 (see Table 1).

Except for specimen 668-68 the zoning is not oscillatory on the scale at which this study was done. The zoning paths of different garnet grains from the same specimen closely overlap so the data can be generalized by grouping together all analyses from the same rock. The zoning paths of the garnets are given in Figure 3. Some of these data are from Brown (1967, p. 283). More data on the Otago garnets are available than have been plotted; the data given are thought to be representative.

Mineral Assemblages and Metamorphic Grade. Mineral assemblages in rocks containing the

TABLE 1. GARNET RIM COMPOSITIONS

Wt %	4-18	4-24	8-31	17-4	668-11	668-15 ^a	668-63	668-186	668-213	668-276
Pyrope ^b	(3.2)	9.5	(3.7)	(5.4)	1.3	1.8	1.03	1.9	1.11	1.6
Almandine	66.0	71.3	64.5	58.5	51.3	52.6	47.0	51.2	44.0	53.1
Spessartine	10.1	0.90	15.4	17.5	13.7	14.1	18.1	15.1	17.2	13.5
Grossularite	20.7	18.4	16.4	18.6	33.1	30.7	33.9	31.9	37.4	31.4
Total		100.1			99.4	99.2	100.0	100.1	99.7	99.6
Mol%										
Pyrope	3.83	11.2	4.45	6.5	1.55	2.15	1.22	2.25	1.32	1.91
Almandine	64.1	68.4	62.8	56.6	49.7	51.1	45.2	49.2	42.3	51.4
Spessartine	9.86	.86	15.1	17.0	13.3	13.8	17.5	14.6	16.6	13.1
Grossularite	22.2	19.5	17.6	19.9	35.4	33.0	36.0	33.9	39.7	33.6
$K_D = \frac{Mg/Fe \text{ gar}}{Mg/Fe \text{ bio}}$.086	.123	.088	.116	.048	.062	.044	.052	

^a From Brown, 1967, p. 283.

^b Parentheses enclose values for pyrope determined by subtracting the sum of the other components from 100.

TABLE 2. BIOTITE ANALYSES

Wt %	4-18	4-24 ^a	8-31	17-4	668-11 ^b	668-15 ^b	668-63 ^b	668-186
SiO	35.5		35.4	35.1	36.4	35.9	35.3	37.2
Al ₂ O ₃	16.0		16.3	16.1	15.2	15.0	15.6	16.1
TiO ₂	1.79		2.06	1.30	1.22	1.10	1.38	1.18
FeO ^c	22.5		21.0	20.8	23.2	22.3	22.6	19.8
MgO	8.54		9.57	11.5	8.45	8.49	7.82	9.76
MnO	0.17		0.21	0.21	0.16	0.22	0.31	0.20
CaO	tr		n.d.	tr	0.25	0.12	0.18	0.05
Na ₂ O	tr		n.d.	tr	0.14	n.d.	n.d.	0.02
K ₂ O	9.76		9.72	9.34	(7.87)	(7.39)	n.d.	9.56
H ₂ O ^d	3.81		3.83	3.85			n.d.	3.87
Total	98.1		98.1	98.2				97.7

n.d. = not determined.

tr = trace.

Si	5.58		5.52	5.47	5.77	5.80	5.71	5.76
Al	2.42		2.48	2.53	2.23	2.20	2.29	2.24
Total	8.00		8.00	8.00	8.00	8.00	8.00	8.00
Al	0.54		0.52	0.42	0.60	0.65	0.68	0.70
Ti	0.21		0.24	0.15	0.15	0.13	0.17	0.14
Fe	2.96		2.75	2.70	3.07	3.01	3.05	2.56
Mg	2.00		2.22	2.67	1.99	2.04	1.89	2.25
Mn	0.022		0.028	0.023	0.02	0.03	0.04	0.023
Total	5.73		5.76	5.97	5.83	5.86	5.83	5.68
Ca					0.04	0.02	0.03	0.01
Na					0.001			0.00
K	1.96		1.94	1.85	(1.59)	(1.52)		1.89
Total	1.96		1.94	1.85	(1.63)	(1.54)		1.90

^a No analytical data are available. $\beta, \gamma = 1.626 \pm .004$. If the total octahedral occupancy is taken to be 5.80 and if $Fe + Mg = 4.56$ (both these figures being similar to those of biotites in comparable rock) then from tables in Trogger (1959, p. 84) $Fe/Fe + Mg = 0.43$, thus $Fe = 1.96$ and $Mg = 2.60$.

^b Biotite in 668-11, -15, -63 may be somewhat weathered. Apparently K_2O has been leached in 11 and 15. See Brown, 1967 (p. 273-4).

^c All Fe has been calculated as FeO .

^d H_2O was not measured but was calculated on the basis of $4(OH)$ per formula unit.

TABLE 3. CHLORITE ANALYSES

	4-18	8-31	668-63	668-11	668-186
SiO ₂	25.8	25.5	27.0	28.4	27.2
Al ₂ O ₃	20.3	21.2	20.2	19.3	19.7
TiO ₂	0.08	.05	0.12	0.07	tr
FeO ^a	29.6	26.3	32.8	31.9	27.1
MgO	11.9	13.4	10.9	10.3	13.6
MnO	0.29	0.42	0.53	0.37	0.41
H ₂ O ^b	11.2	11.2	11.5	11.4	11.3
Total	99.1	98.1	103.0	101.8	99.3

Si	2.78	2.73	2.82	2.98	2.87
Al	1.22	1.26	1.18	1.02	1.13
Total IV	4.00	4.00	4.00	4.00	4.00

Al	1.34	1.40	1.31	1.37	1.33
Ti	.004	.003	0.009	0.004	
Fe	2.66	2.36	2.87	2.80	2.39
Mg	1.90	2.13	1.70	1.61	2.14
Mn	0.026	0.035	0.043	0.031	0.034
Total VI	5.93	5.93	5.92	5.82	5.90

^a All Fe has been calculated as FeO.

^b H₂O was not measured but was calculated on the basis of 8(OH) per formula unit.

analysed garnets are given in Table 4. Garnets from Otago are associated with the following minerals which indicate low grade: stilpnomelane, albite plus epidote, and actinolite. Also suggestive of low grade in this area is the abundance of chlorite and sparsity of biotite (see Brown, 1967, p. 263). In the Otago region, metamorphic grade increases slightly to the northeast, across a biotite isograd. Figure 4a shows the location of the garnet specimens relative to this gradient. The Vermont specimens, 8-7 and 8-31 (Fig. 4b), are from the biotite and garnet zones respectively, according to Christman and Secor (1961). 8-31 contains the pair albite-epidote and only a very small amount of garnet is present (<1-2%). The metamorphic grade of this specimen is probably not greatly different from that of the biotite zone rocks of Otago. The specimens from Scotland, 4-18 and 4-24, are from the biotite and garnet zones respectively in the Loch Lomond area (Tilley, 1925, Fig. 4c present report). 4-18 contains albite-epidote and the garnet is sparsely developed. The grade seems to be comparable to that of 8-31. In 4-24 the garnet is distinctly more plentiful, being present in porphyroblasts 1-2mm diameter and making up about 5 percent of the rock. Most adjacent rocks, though of varied lithology, have similarly prominent garnets. One other specimen from the same locality as 4-24 contains the pair albite-oligoclase, indicating a somewhat higher grade for 4-24 (cf. Crawford, 1966) than that of the other specimens of this report. The one specimen from the Cascades, 17-4, occurs in what could be classified as albite-epidote-amphibolite facies, or transitional between the greenschist and amphibolite

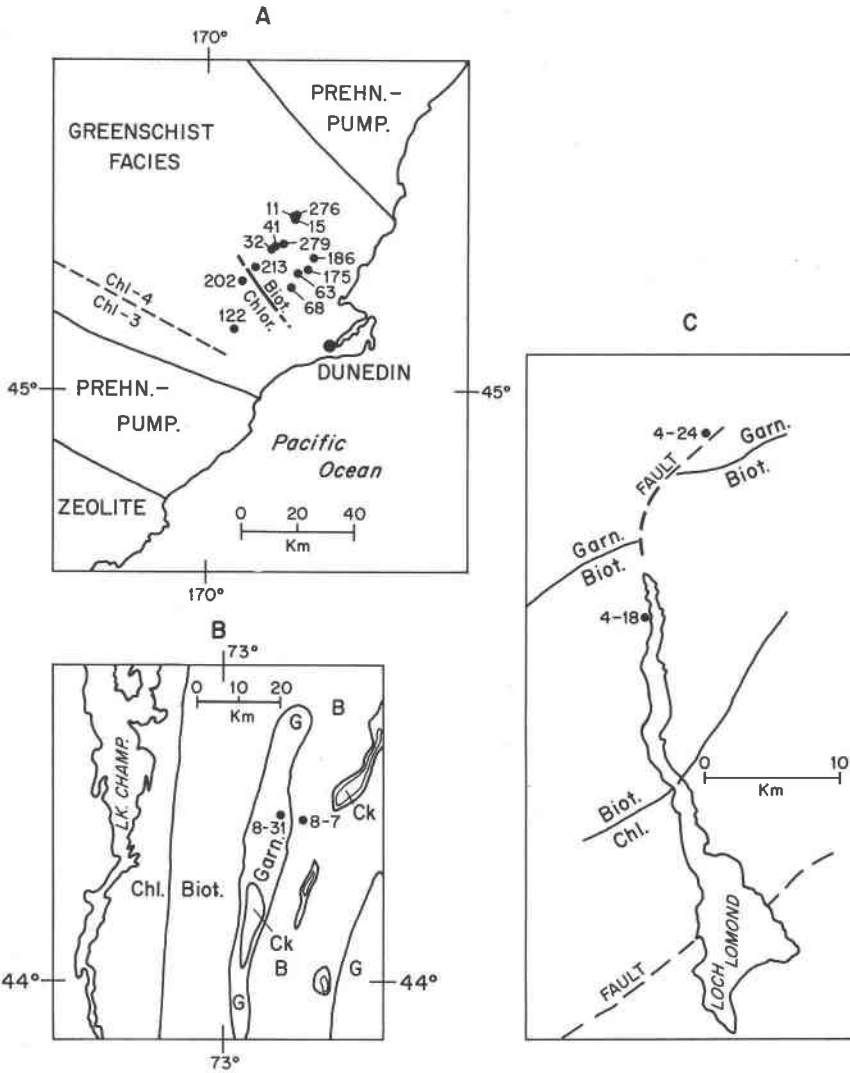


FIG. 4. Locality Maps. A. Eastern Otago, New Zealand. A map showing metamorphic zones in the whole of the South Island of New Zealand is given by Landis and Coombs (1967, p. 503). Prefix no. is 668. B. Western Vermont, U.S.A. The metamorphic zones are from the Geologic map of Vermont 1961; Doll ed. The zones shown here are chlorite, biotite, garnet and chloritoid-kyanite. Localities for 7 and 31 correspond to localities 7 and 16 respectively in Christman and Secor (1961, p. 15). C. Loch Lomond, Scotland. The metamorphic zones are from Tilley (1925).

TABLE 4. MINERAL ASSEMBLAGES

	4-18	4-24	8-7	8-31	17-4	668-11	668-15	668-37	668-41	668-63	668-68	668-122	668-175	668-186	668-202	668-213	668-276	668-279
Quartz	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Albite	M	M	M	M	M	M	M	M	A	M	M	M	M	M	M	M	M	M
Epidote	M	A	M	M	M	M	M	M	M	A	M	A	M	M	M	M	M	A
Muscovite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Chlorite	M	A	M	M	A	A	A	M	M	M	M	M	M	M	M	A	A	M
Biotite	M	M	M	M	M	A	M	M	M	A	M	M	M	M	M	M	A	M
Stilpnomelane	M	M	M	M	M	M	A	M	M	M	M	M	M	M	M	M	A	M
Actinolite	M	M	M	M	M	M	A	M	M	M	M	M	M	M	M	M	A	M
Hornblende	M	M	M	M	M	M	A	M	M	M	M	M	M	M	M	M	A	M
Garnet	A	M	A	A	M	A	M	A	M	M	M	M	M	M	M	M	A	M
Calcite	M	A	A	A	A	M	M	A	M	M	M	M	M	M	M	M	A	M
Ilmenite	A	A	A	A	A	M	M	M	M	M	M	M	M	M	M	M	A	M
Rutile	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Sphene	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Graphite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Pyrite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Pyrrhotite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Chalcopyrite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M
Magnetite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	A	M

A = Accessory Constituent (<1-2%) M = Major Constituent (>1-2%)

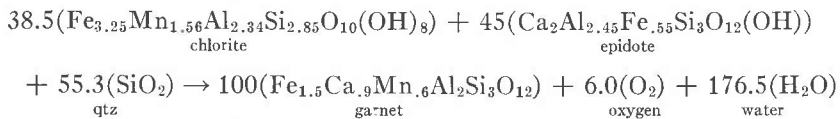
facies (Turner, 1968, p. 302-7). Albite, epidote and hornblende¹ are present in this specimen. The rock comes from the Cascade River Schist (Misch, 1966) along highway 16 about 6 miles northeast of Marblemount, Washington.

Almost all the specimens reported here are quartzo-feldspathic schists, probable derivatives of greywacke-type sandstone. The only other rock type, represented by specimens 668-41, -122, -202, -279, is manganiferous and very rich in quartz. Probably these quartzose rocks were originally manganiferous cherts.

The distribution coefficient for Fe and Mg between biotite and garnet is given in Table 1. K_D (Mg/Fe)(gar/biot) for the Otago rocks is smaller than that reported by other workers (Albee 1965, Heitanen 1969), probably because of the comparatively low grade of these rocks. However, as demonstrated by Albee (1965), this K_D is also dependent upon compositional factors, and for this reason a detailed correlation of K_D with grade is not attempted here. It should be noted that the rim compositions of garnets have been used for the calculation of K_D given in this report, an improvement over using bulk garnet compositions of zoned garnets.

INTERPRETATION

A Possible Garnet-Producing Reaction. Undoubtedly many different reactions produce garnet. The reaction which occurs in any given rock depends on several factors, such as lithology, grade, P_{O_2} etc. In many rocks of the greenschist facies the present mineral assemblage is: quartz-albite-epidote-muscovite-chlorite-garnet (plus accessories). Assuming a closed system except for water and oxygen it seems that the garnet in this assemblage grew from the breakdown of epidote, the only source of Ca, plus an Fe-Mn component of chlorite. The following reaction has been balanced after having assigned the garnet composition to 50 mole percent almandine, 30 grossularite, and 20 spessartine, comparable to the rim composition of some Otago garnets. The epidote composition was set at 18 percent of the Fe end-member, comparable to common Otago epidotes.



The chlorite used up in this reaction is an Fe-Mn chlorite *component* of the natural chlorite. The writer envisages a process whereby the actual chlorite recrystallizes during reaction and, in so doing, contributes an Mn-Fe chlorite component, as shown in the above equation, to the formation of the garnet. Thus, the production of garnet would lead to a more Mg-rich chlorite besides a reduced amount of chlorite. The reaction is

¹ The amphibole is identified as hornblende on the basis of a chemical analyses: SiO₂ = 44.7, Al₂O₃ = 11.9, TiO₂ = 0.35, total Fe as FeO = 18.0, MgO = 9.5, MnO = 0.31, CaO = 11.0, Na₂O = 1.06, K₂O = 0.61.

not strictly correct as written because no provision is made for change in X_{Mg} and X_{Mn} in coexisting muscovite and X_{Mn} in epidote which must accompany changes in these values in the chlorite in order for chemical equilibrium to be maintained. Thus some Mn epidote and some Mn-Fe muscovite should also break down. The amount of muscovite involved would be very small considering the small amount of garnet produced and also the relatively strong fractionation of Mn and Fe between chlorite and muscovite. However, if *any* muscovite breaks down K must be released from solid phase system since no new K phase is formed. The reaction as written uses chlorite with an X_{A1} about equal to that of existing chlorites so that no adjustment in X_{A1} of coexisting muscovite would be required.

An attempt has been made to determine the slope on a P - T graph of the equilibrium line for the above reaction by evaluating the equation:

$$\int_{P_1}^{P_2} \Delta V dP = \int_{T_1}^{T_2} \Delta S dT$$

The curve is arbitrarily taken to pass through the point $P=5000$ bars, $T=400^\circ\text{C}$. The molar volumes of epidote, chlorite, and garnet were calculated by dividing the molecular weight by the density. The density of each mineral was estimated from graphs in Tröger (1959). Substitution of Mn for Fe was assumed to have negligible affect on the density of chlorite. The molar volume of quartz was taken from Robie (1966, p. 446). The volumes used are listed in Table 5. It was assumed that ΔV_{solids} does not change appreciably between atmospheric and metamorphic conditions. Thus:

$$\int_{P_1}^{P_2} \Delta V dP = \Delta V_{\text{solids}} \Delta P + \int_{P_1}^{P_2} V_{H_2O} dP.$$

The integral of $V_{H_2O} dP$ was evaluated graphically at 400°C using the data of Kennedy and Holser (1966, p. 377). The oxygen in the reaction has been treated as water. Values calculated are given in Table 5.

For ΔS of the reaction it was considered that a reasonable approximation could be made by using the entropy of hydration alone (see Fyfe *et al*, 1958, p. 116). Values for ΔS_{hyd} were taken either directly from the graph in Fyfe *et al* (*ibid.* p. 118) or where $P > 2500$ bars values were extrapolated from this graph (see Table 5). It was assumed that at any given pressure ΔS_{hyd} could be considered constant over ΔT inasmuch as ΔT is so small. Thus, starting at $P=5000$ bars, $T=400^\circ\text{C}$ points on the curve were calculated using the relationship:

TABLE 5. DATA USED IN CALCULATION OF THE SLOPE OF THE EQUILIBRIUM CURVE FOR THE REACTION CHLORITE+EPIDOTE+QUARTZ→GARNET+WATER.
SEE TEXT FOR EXPLANATION OF CALCULATION

P_2 bars	ΔV_{solid}	$\Delta V_s \Delta P$	$P_1 \int^{P_2} V_{\text{H}_2\text{O}} dP$	$P_1 \int^{P_2} \Delta V dP$	ΔS_{hyd}^a	ΔS_{hyd}	$\Delta T^\circ\text{C}$
	cc/mole garnet	cc bars mole garnet	cc bars mole garnet	cc bars mole garnet	Cal deg. mole H ₂ O	cc bars deg. mole garnet	
4000	-42.8	42800	- 35,700	7,100	11	835	+ 8.5
3000	-42.8	85600	- 73,000	12,600	11.5	875	+14.4
2000	-42.8	128500	-112,700	15,800	12.0	913	+17.3
1000	-42.8	171500	-156,500	15,000	13.0	988	+15.2

	Mineral	Molar Volume cc/mole
$P_1 = 5000$ bars	Chlorite	224.3
$T_1 = 400^\circ\text{C}$	Epidote	140.4
	Quartz	22.7
	Garnet	119.3

^a From Fyfe *et al.*, 1958, p. 118.

$$\Delta T = \frac{\Delta V_{\text{solids}} \Delta P + \int_{P_1}^{P_2} V_{\text{H}_2\text{O}} dP}{\Delta S_{\text{hyd}}}$$

The resulting equilibrium line is given on Figure 5. It is noteworthy that the line is slightly negative in slope above 2000 bars. The slope of the line calculated from a starting point of 300°C and 5000 bars is slightly more negative; starting at 500° the slope is slightly positive. Possibly the reactions by which biotite and oligoclase are produced, which occur at about this same grade, have positive slopes, so that at high pressure garnet would appear before these minerals (cf. Turner 1968, p. 307).

It should be emphasized that the above reaction, though perhaps approximately correct for many rocks, requires modification in order to be applicable to the majority of garnet bearing rocks in the greenschist facies, which contain one or more of the minerals: biotite, stilpnomelane, actinolite, and calcite. These minerals would be involved in the reaction. One such likely reaction for a biotite bearing rock is:



Given complete data on the composition of coexisting minerals and with the aid of matrix algebra (*e.g.* Perry, 1967) it should be possible to accurately specify the nature of reactions such as this one.

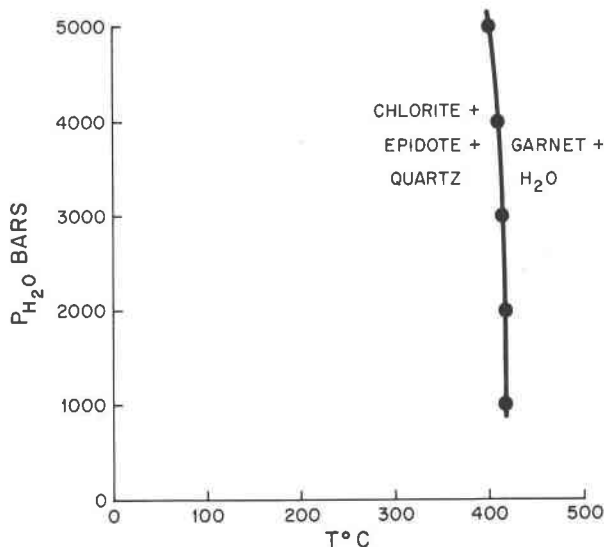


FIG. 5. Calculated slope of the equilibrium curve for the reaction: chlorite+epidote+quartz→garnet+H₂O. See text for a more precise description of the reaction and also for the method of calculation. The curve has been arbitrarily located to pass through the point at $P=5000$ bars, $T=400^{\circ}\text{C}$.

The Controls of Zoning Paths. The zoning paths of garnets (given in Fig. 3) generally move, going from core to rim, away from spessartine and toward almandine. This zoning may result from either or both of two controls: 1) depletion of Mn from the equilibrium system during garnet growth; 2) increase with progressive metamorphism in percent almandine stable in garnet. Hollister (1966) and Atherton (1968) have demonstrated the importance of Mn depletion in controlling the zoning of garnets from contact and regional metamorphic terrains respectively. This model assumes that the garnets have compositional freedom at any given metamorphic grade.

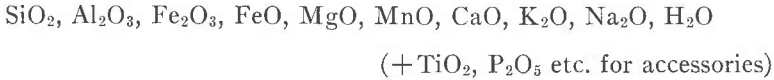
a. Garnets Invariant at Constant Grade

For four of the specimens of the present study it seems unlikely that the garnets do in fact have any degree of compositional freedom at constant grade. Specimens 668-11, 15, 213, 276, all contain the assemblage:²

² 213 also contains calcite. 276 contains calcite and lacks chlorite but does contain chlorite-vermiculite which is almost certainly derived from primary chlorite (Brown *ibid.*, p. 273).

Quartz-albite-epidote-muscovite-chlorite-biotite-stilpnomelane-
actinolite-garnet (plus accessories)

The components necessary to make up these phases and express their possible compositional variations are:



Thus assuming water vapor to be present during metamorphism there are a total of ten phases and ten components. At one metamorphic grade all the phases should be invariant in composition. In fact, the garnets in these assemblages are zoned (Fig. 6). If all the phases were associated in equilibrium during garnet growth then the zoning represents the control of metamorphic grade only, and presumably an increase in grade. The more almandine-rich garnet grows later and thus at higher grade. This argument is strengthened by two other observations: 1) The zoning paths of all four garnets coincide, whereas garnets from other assemblages are zoned quite differently. This is a necessary condition for the above hypothesis to be valid and further seems strong evidence that the garnets crystallized in approximate equilibrium with coexisting minerals. 2) The garnets which have higher almandine content on the rim are actually from higher grade. All four garnets are from the biotite zone but 276, 15, 11 with about 52 percent almandine on the rim come from some 20 km. upgrade from the biotite isograd, whereas 213 with 44 percent almandine is only 2 km. from the isograd (Fig. 4a).

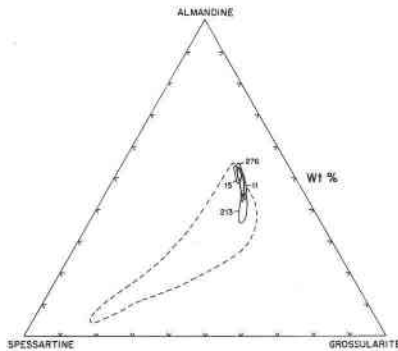


FIG. 6. Zoning paths for garnets which should, according to the phase relationships, be invariant in composition at constant grade. The dashed line shows the compositional range of Otago garnets.

b. Garnets Which are Variable at Constant Grade

Other garnets cannot be interpreted in the above fashion because there are too few coexisting phases for compositional invariance to be required at constant grade. Interpretation of the zoning paths of these garnets is difficult and what follows is offered only as a tentative explanation of *some* of the observable features. There seems little doubt that much of the zoning occurs at constant grade and is caused by Mn-depletion in the garnet producing mineral (e.g. Atherton, 1968). Presumably the growth of the garnet at constant grade at some localities results from considerable overstepping of a garnet producing reaction (compare with Yoder, 1952, p. 623).

Some aspects of the zoning paths are common to many garnets. One such feature is the tendency for the zoning path of garnet in any one specimen to lie at more or less constant percent of grossularite, even though garnets from different specimens contain different amounts of grossularite (Fig. 3). In many of these rocks the only sources of the material required for garnet production are chlorite and epidote. The compositional relationships among chlorite, epidote and garnet, shown on Figure 7, are such that the percent grossularite produced depends on the Al-content of the chlorite and epidote which decompose to make the garnet. Al-rich chlorite and epidote produce Ca-poor garnet. If the Al-content of the chlorite and epidote is constant during garnet growth the grossularite content will be constant also. Possibly the Al content of these minerals would be kept more or less constant by interaction with muscovite (see above). If this relationship is valid then the grossularite content of the garnet would be closely related to the activity of Al in the host rock: the higher the activity of Al relative to that of Fe and Mn, the poorer the garnet is in grossularite.

Some of the garnets from Otago which occur in low-grade, Mn-rich rocks (668-122, -202) have zoning paths which show an increase in grossularite from core to rim. This would be possible in an Mn² component of epidote is breaking down so that the remaining epidote becomes enriched in Ca³.

Another characteristic of the zoning paths of many garnets is a bend upward away from grossularite, toward almandine, near the garnet rim (Spec. 17-4, 4-18). Atherton's data (1968, p. 354) show a similar feature which he interprets to be due to a decrease in temperature. There would seem to be at least two possible explanations for this phenomenon: 1) During garnet growth there could be a change in the phases involved in the garnet producing reaction. Possibly the reaction epidote plus chlorite

³ It is assumed that Mn⁺² substitutes for Ca in the epidote.

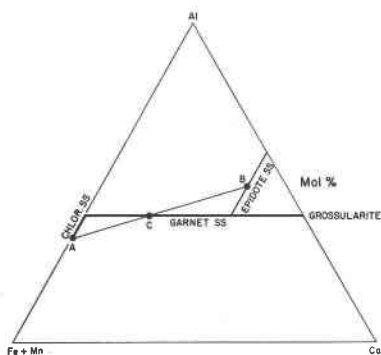


FIG. 7. Illustration of the compositional relationships for the reaction:

chlor. (A) + epidote (B) → garnet (C)

If the reactants contain more Al the garnet produced contains less grossularite.

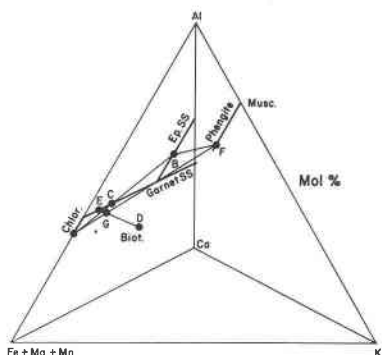


FIG. 8. Illustration of the compositional relationships for the reaction:

chlorite (A) + epidote (B) + muscovite (C) → biotite (D) + garnet (E)

The garnet produced in this section contains less gross than that shown in Fig. 7 although the chlorite and epidote used have the same composition. The Al-Ca-Fm triangle is the same as that in Fig. 7. Phengite and biotite lie in the Al-K-Fm triangle. G = bulk composition of the reacting system. G lies in the triangle: chlorite-phengite-epidote, and also on the line joining biotite and garnet.

going to garnet changes to the reaction epidote plus chlorite plus muscovite going to biotite plus garnet. Figure 8 shows how the second reaction could produce a garnet poorer in grossularite than the first. 2) The distribution coefficient of Al among coexisting phases could change in response to changes in grade. For example, relatively more aluminous component of chlorite and epidote could begin to break down to produce garnet with less grossularite and chlorite and epidote with less aluminum. This possibility seems less likely than the first inasmuch as analyses of chlorite show no tendency for the Al-content to decrease with increase grade (e.g. Table 3, also Brown, 1967, p. 271). Whatever the cause of this bend toward almandine it would seem to be best correlated with an *increase* in temperature considering that many geologists have observed that the almandine content of garnet shows a general tendency to increase with grade (e.g. Sturt, 1962). If this concept is valid then the garnets with this type of zoning path have grown first at constant grade, maintaining more or less constant percent grossularite with compositional variations controlled by Mn depletion. Then relatively late in the

growth history increased grade changes the nature of the reaction and leads to production of garnet with less grossularite. Thus both Mn-depletion and change in grade have controlled the zoning path.

It might be argued that the bend toward almandine in fact represents the initiation of Ca-depletion (L. S. Hollister, oral communication, 1968). Assuming that garnet grows for the most part from chlorite and epidote, the strong fractionation of Mn in garnet with respect to chlorite, the Mn reservoir, leads to decreased activity of Mn in the equilibrium system as garnet grows and seals off successive layers of Mn-rich material. However, activity of Ca in the Ca reservoir, epidote, is essentially fixed or may increase somewhat as Mn activity goes down. As long as epidote is supplying the Ca there seems to be no good mechanism for reducing the activity of Ca in the equilibrium system.

The zoning of garnet in 8-31 is anomalous (Fig. 3). The core is richer in almandine than the rim. The rim and core are not at all gradational, and in fact in thin section it can be seen that the two zones are separated by a distinct Becke line. This core is apparently relict detrital garnet. The rim is comparable in composition to other garnet grains in the same specimen which lack the almandine rich core. The zoning in the non-detrital garnet is unusual in that during initial growth the grossularite content increased while almandine and spessartine decreased.

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