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Zoned garnets in some Scottish Dalradian pelites

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ABSTRACT. Zoning in garnets in Barrovian garnet zone rocks of central Perthshire is shown to be dependent on the continuous prograde reaction histories in which the garnet was involved. In highly aluminous rocks, garnet grows at the expense of chloritoid and staurolite whereas in less aluminous rocks garnet grows at the expense of chlorite. Minerals included in garnet such as ilmenite, plagioclase, chlorite, and chloritoid show compositional changes which with the garnet zoning elucidate the garnet-forming reactions. Where garnet is resorbed to produce staurolite the former loses Fe at its rim to staurolite so that 'reverse' zoning of decreasing Fe and increasing Mn and Ca towards garnet rim develops.

SEVERAL models have been invoked to explain the zoning patterns in garnets. Growth with frozen equilibrium partitioning during metamorphism (Harte and Henley, 1966), preferential fractionation or segregation of certain elements in the matrix (Hollister, 1966; Atherton, 1968), and diffusion models involving ion exchange between garnet and the surrounding reservoir (Anderson and Buckley, 1973) have been advanced. More recently zoning in garnets reflecting supposed continuous and discontinuous reactions has been popular (Tracy *et al.*, 1976; Crawford, 1977; Trzeienski, 1977; Thompson *et al.*, 1977). This account proposes that the garnet zoning described is produced and modified by the reactions in which garnet is produced or consumed.

Geological setting

The rocks examined belong to the central Perthshire garnet zone in the classic Barrovian zonal sequence. Details and locations of the samples are given in Sivaprakash (1979) and in fig. 1. The rock types in the area are mainly garnetiferous mica schists (Pitlochry Schists), hornblende schists (Green Beds) of clastic and, or, of igneous origin, and metamorphosed basic intrusions and lavas (epidiorites). This study is mainly concerned with the garnets from metapelites. These rocks range in metamorphic grade from just above the garnet isograd (Atherton, 1968) to beyond where staurolite and kyanite first appear, the grade of metamorphism in the area generally increases towards the north or north-west.

Metapelites are strongly schistose, highly micaceous rocks with 2 to about 20% of euhedral garnets. In the greater part of the area, the rocks consist of quartz + muscovite + biotite + chlorite + garnet ± plagioclase ± tourmaline ± ilmenite ± rutile ± other accessories. Biotite may be locally absent. Staurolite alone joins the above assemblage at Weem whereas staurolite and kyanite join at Grandtully. These staurolite- and kyanite-bearing rocks are not widespread beyond Weem to Grandtully. Paragonite coexists with muscovite in some rocks, but chloritoid, and margarite are included in garnet porphyroblasts and are not present in the matrix (e.g. rocks from Grandtully). Chloritoid occurs only in highly aluminous rocks with low bulk Mg/(Mg + Fe) (Sivaprakash, 1979).

Garnet porphyroblasts in metapelites are strongly idioblastic and range in diameter from < 1 mm to > 6 mm. Both inclusion-free and inclusion-bearing types occur, the latter being commoner. Most of the garnets grew during static crystallization (M3 metamorphism, post F2 deformation of Johnson, 1963), but rarely some S-shaped inclusions are present indicating some syntectonic crystallization. Quartz, ilmenite, rutile, and white micas are the common inclusions. Occasionally chloritoid, staurolite, tourmaline, and graphite are included. Most of the garnets do not show any signs of retrogression but where retrograded, chlorite and biotite fill fractures and the rims of garnet. Garnets in staurolite-bearing rocks show signs of resorption (fig. 2) where staurolite and biotite replace the garnet rim.

Although the lowest-grade garnets are fine grained (0.5 to 1 mm in diameter) and large garnet porphyroblasts (4 to 6 mm) are present in higher-grade rocks such as kyanite-bearing types, the increase in size of the garnets with increase in

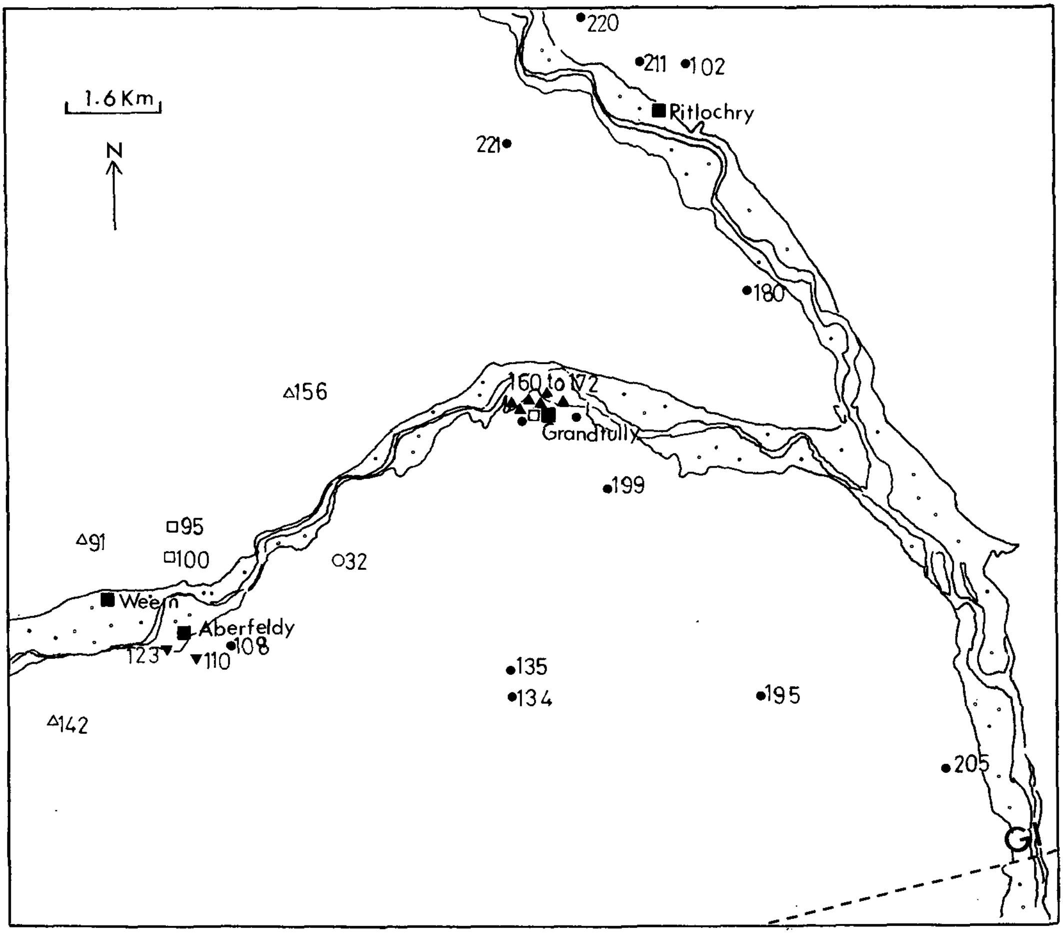


FIG. 1. Locations of samples. GI: Garnet isograd (Atherton, 1968); filled circles: quartz + muscovite + biotite + chlorite + garnet ± plagioclase ± opaques ± tourmaline (= assemblage I); inverted triangles: assemblage I without biotite; open squares: assemblage I with staurolite; filled triangles: assemblage I + staurolite + kyanite; open circle: assemblage I without biotite but with staurolite and kyanite; open triangles: hornblende schists. The areas hatched with small open circles represent the river valleys of the Tay and Tummel.

metamorphic grade is not systematic. The size and volume of garnet are related to the bulk compositions. Hornblende schists and carbonaceous metapelites have low contents of garnets which are small (about 0.5 mm or less).

Garnet zoning

Garnet analyses were carried out by the EDS methods of Statham (1976) with the correction procedures of Sweatman and Long (1969). Detailed analyses of garnets are presented elsewhere (Sivaprakash, 1979). Garnet compositions are shown on a ternary (Ca + Mn)-Fe-Mg diagram (fig. 3). All garnets have cores relatively richer in Ca + Mn and rims richer in Fe + Mg, some garnet rims (e.g. 100, 164, 169, 170, 171) show high Mg/Fe relative to other garnet rims so that a crossing of the 'tie lines' occurs (fig. 3). Such high Mg/Fe in garnet rims occurs in all staurolite-bearing rocks. The reason for this becomes clear when zoning is discussed.

Most of the garnets probed show 'normal' zoning with decreasing Mn and Ca and increasing Fe and Mg from core towards rim. In order to understand the garnet-forming reaction, phase relations in some pelitic rocks are shown on a Thompson AFM projection in fig. 4. This figure depicts the phase relations in rocks in which the garnet + chlorite tie line is still compatible, i.e. rocks in which biotite does not coexist with staurolite, kyanite, and chloritoid. The detailed chemistry of

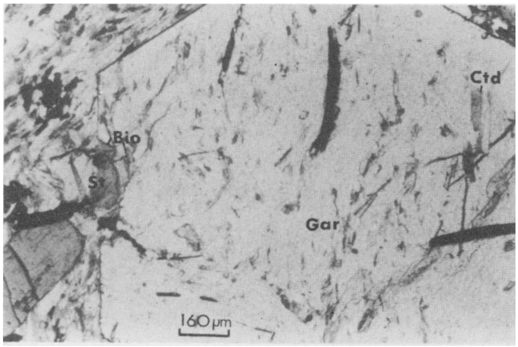


FIG. 2. Photomicrographs showing the garnet (Gar) resorption texture. Staurolite (St) + biotite (Bio) replace garnet rim. Chloritoid (Ctd) inclusions are present in the garnet porphyroblast but not in the matrix (sample 171).

the phases involved is discussed in Sivaprakash (1979). The three-phase association garnet + chlorite + biotite(+ muscovite + quartz) is common over a large area. The mineral compositions (with garnet, the rim compositions) show continuous increase in Mg/(Mg + Fe) with increase in metamorphic grade. The three-phase garnet-chlorite-biotite triangle moves towards M with increase in grade. This defines a continuous reaction by which garnet appears and increases in modal abundance at the expense of chlorite:

$$\text{chlorite} + \text{muscovite} + \text{quartz} = \text{garnet} + \text{biotite} + H_2O \quad (1)$$

Thompson (1976) calibrated qualitatively the relative isobaric temperatures (T) for the Mg, Fe, Mn end-members in various reactions in AFM system. For reaction (1) $T_{Mg} > T_{Fe} > T_{Mn}$. In other words, T of the reaction with the Mg end-member in the system is higher than with Fe which is higher than with Mn. The observed 'normal' zoning of Mn decreasing and Mg/(Mg + Fe) increasing from core towards rim is consistent with the growth of garnet by reaction (1). Further, the following individual examples of garnets and the compositions of inclusions preserved in them show that garnet zoning is influenced by the continuous-discontinuous reactions in which the garnet is involved.

I. In rock 134 garnet contains ilmenite inclusions. Ilmenite is not present in the matrix. Ilmenite inclusions in garnet have continuously decreasing Mn-content towards garnet rim, sympathetic with the garnet itself (fig. 5). Rutile inclusions are present at the garnet rim and in the matrix so that the continuous reaction (1) now involves ilmenite:

$$\text{chlorite} + \text{muscovite} + \text{ilmenite} + \text{quartz} = \text{garnet} + \text{biotite} + \text{rutile} + H_2O \quad (1a)$$

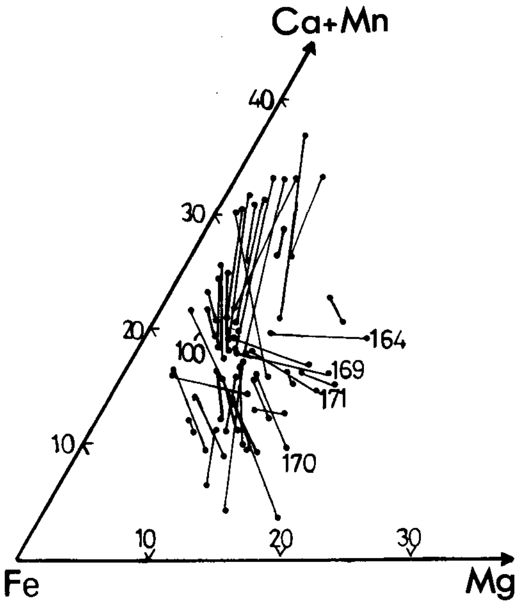


FIG. 3. Part of an ionic (Ca + Mn)–Fe–Mg diagram showing the garnet compositions in metapelites. Garnet core and rim compositions are joined by tie lines except where the core and rim compositions are not separately determined. In each tie line the top or the left-end of the line represents the garnet core composition and the bottom or the right-end of the line represents the garnet rim composition. Numbers shown are the sample numbers (garnets from staurolite-bearing rocks) referred to in the text.

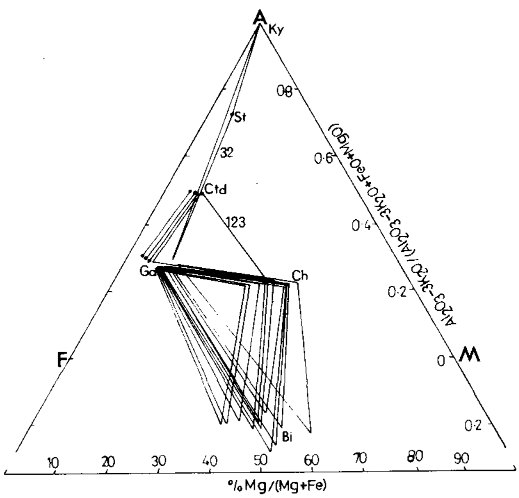
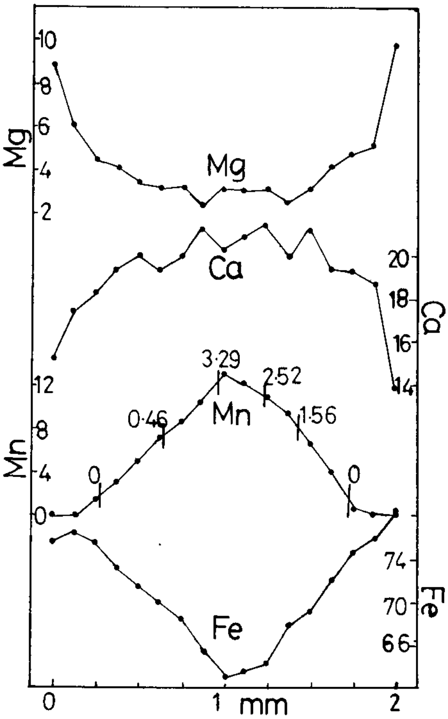
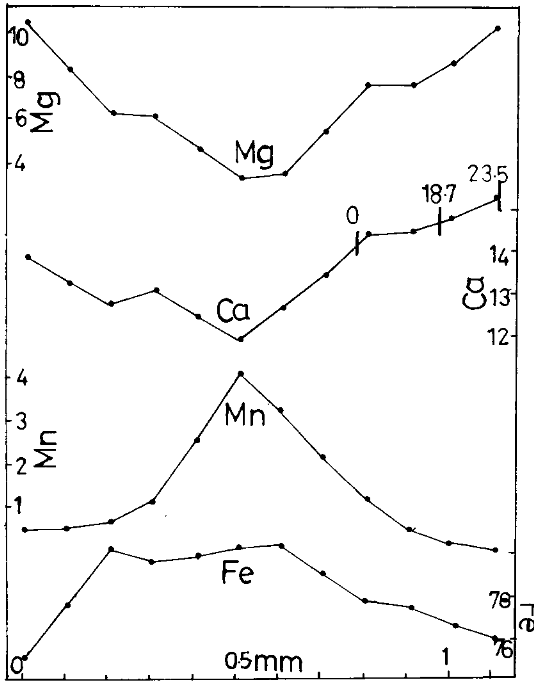


FIG. 4. AFM projection showing phase relations in metapelites in which the garnet–chlorite tie line is compatible. Bi: Biotite; Ch: Chlorite; Ctd: Chloritoid; Ga: Garnet; Ky: Kyanite; St: Staurolite.





FIGS. 5 and 6. FIG. 5 (*left*). Compositional profile of garnet in sample 134. Ionic per cent Mg, Ca, Mn, Fe plotted against distance. Vertical bars on the Mn profile indicate the locations of ilmenite inclusions in garnet. Numbers on the vertical bars correspond to %Mn/(Mn + Mg + Ca + Fe) of ilmenites. FIG. 6 (*right*). Compositional profile of garnet in sample 135. Ionic per cent Mg, Ca, Mn, Fe plotted against distance. Vertical bars on the Ca profile indicate the locations of plagioclase inclusions in garnet. Numbers on the vertical bars correspond to %Ca/(Ca + Na) of plagioclase.

Thus garnet derives some Mn from ilmenite. Ilmenite decreases in modal abundance and finally disappears.

II. In rock 135 there is 'reverse' zoning in Ca and Fe, where garnet Ca increases and Fe decreases towards the rim (fig. 6). This garnet has plagioclase inclusions. Although these inclusions are only sparse, it is evident that they show an increase in anorthite content towards the garnet rim. The continuous reaction (1) will now involve plagioclase:

$$\text{chlorite} + \text{muscovite} + \text{quartz} + \text{plagioclase}_1 = \text{garnet} + \text{biotite} + \text{plagioclase}_2 + H_2O \quad (1b)$$

by which plagioclase decreases in modal abundance. Ca and Fe are antipathetic to each other in garnet structure, so that as Ca increases towards garnet rim, Fe decreases causing the observed 'reverse' zoning.

III. In rock 110 there is no biotite. Chlorites included in garnet show an increase in Mg/(Mg + Fe) towards the garnet rim (fig. 7). The maximum 100 Mg/(Mg + Fe) of included chlorite is 22 as

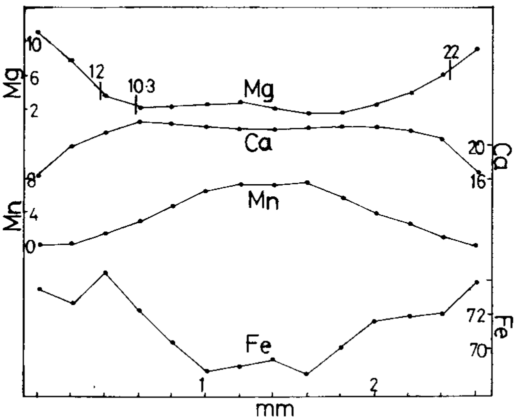


FIG. 7. Compositional profile of garnet in sample 110. Ionic per cent Mg, Ca, Mn, Fe plotted against distance. Vertical bars on the Mg profile indicate the locations of chlorite inclusions in garnet. Numbers on the vertical bars correspond to %Mg/(Mg + Fe) of chlorites.

compared with matrix chlorite of 53. This defines the net continuous reaction:

$$\text{chlorite} + \text{quartz} = \text{garnet} + H_2O \qquad (2)$$

by which garnet appears at the expense of chlorite.

IV. In rock 123 there is no prograde biotite and the garnet contains chloritoid inclusions. This garnet is too irregular for a compositional traverse, but it does show increase in Mg/(Mg+Fe) along with adjacent chloritoid towards the garnet rim. The chloritoid-garnet tie line moves towards M on AFM diagram (fig. 4). There is also chlorite in the rock so that garnet grows by the continuous reaction:

$$\text{chloritoid} + \text{chlorite} + \text{quartz} = \text{garnet} + H_2O \qquad (3)$$

For this reaction $T_{Mg} > T_{Fe} > T_{Mn}$ so that Mn decreases and Mg/Fe increases towards garnet rims.

V. In rock 32 there is neither biotite nor prograde chlorite. This rock has the assemblage garnet + staurolite + kyanite, and some retrograde chloritoid is present in the matrix. Some staurolite is included in the garnet in addition to being present in the matrix. Staurolite which is included in garnet has a lower Mg/(Mg+Fe) than matrix staurolite so that garnet grows by a continuous reaction:

$$\text{staurolite} + \text{quartz} = \text{garnet} + \text{kyanite} + H_2O \qquad (4)$$

Since this is a highly aluminous rock, some chloritoid would also have been present at low grades, so that staurolite itself appears at the expense of chloritoid:

$$\text{chloritoid} + \text{quartz} = \text{staurolite} + \text{garnet} + H_2O \qquad (5)$$

Garnet growth involving chloritoid and staurolite is better documented in a number of rocks at Grandtully (e.g. 164, 170, 171). A representative garnet is sketched in fig. 8. This garnet contains chloritoid and staurolite inclusions. Staurolite inclusions are present near the rim of the garnet whereas chloritoid inclusions are present near the core. Chloritoid is absent in the matrix. Although biotite occurs in the matrix, it is not found included in garnet and in contact with chloritoid. Presumably garnet + chlorite compatibility was not broken as long as chloritoid formed part of the equilibrium assemblage in the rock. Chloritoid inclusions in garnet show increasing Mg/(Mg+Fe) towards the garnet rim (fig. 8). Since chlorite was also present in the low grade, garnet grew at the expense of chloritoid by a continuous reaction:

$$\text{chloritoid} + \text{chlorite} + \text{quartz} = \text{garnet} + H_2O \qquad (6)$$

Further towards the rim, staurolite appears and chloritoid disappears by a discontinuous reaction:

$$\text{chloritoid} + \text{quartz} = \text{staurolite} + \text{garnet} + \text{chlorite} \qquad (7)$$

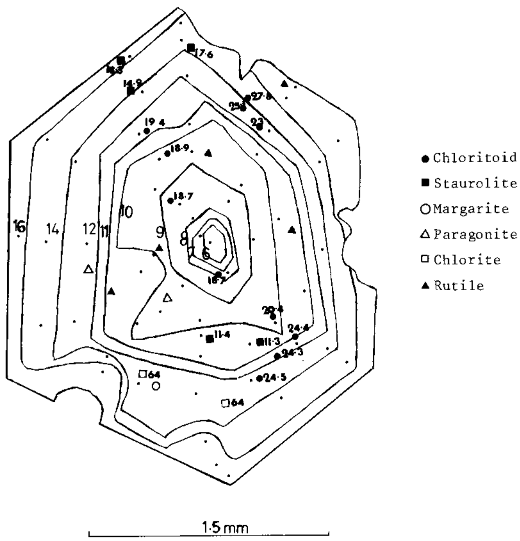


FIG. 8. Sketch of a garnet porphyroblast in sample 171 showing contours of %Mg/(Mg+Fe) and locations of inclusions. Values of %Mg/(Mg+Fe) of garnet (larger thin numbers), and of included ferromagnesian phases (smaller thick numbers adjacent to their locations) are given. Dots represent points of analyses of garnet.

Staurolite included in garnet shows increase in Mg/(Mg+Fe) towards the garnet rim (fig. 8) so that garnet continued to grow until it reached its present size by a continuous reaction:

$$\text{staurolite} + \text{chlorite} + \text{quartz} = \text{garnet} + H_2O \qquad (8)$$

Reactions (6) and (8) have $T_{Mg} > T_{Fe} > T_{Mn}$ so that the garnet has decreasing Mn, and increasing Mg/(Mg+Fe) towards the garnet rim.

In this rock (171) staurolite + biotite is present in the matrix of the rock. Such staurolites are more magnesian than those included in garnet. The staurolite + biotite assemblage is also present in other rocks (95, 100) that do not have chloritoid or low-magnesian staurolites as inclusions in garnets.

Although a continuous reaction:

$$\text{chlorite} + \text{muscovite} = \text{staurolite} + \text{biotite} + H_2O \qquad (9)$$

could produce staurolite + biotite in the matrix, mineral textures (fig. 2) show that garnet was resorbed in the production of staurolite. Possible continuous reactions involved in the production of staurolite at the expense of garnet are:

$$\text{garnet} + \text{muscovite} + H_2O = \text{staurolite} + \text{biotite} + \text{quartz} \qquad (10)$$

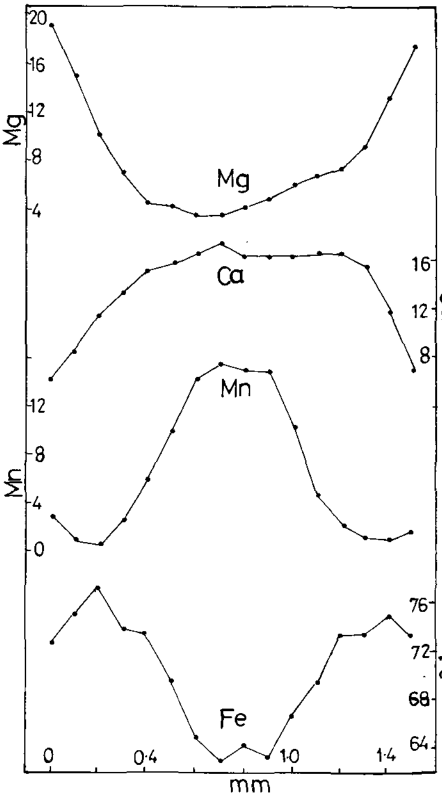
$$\text{garnet} + H_2O = \text{staurolite} + \text{chlorite} + \text{quartz} \qquad (11)$$

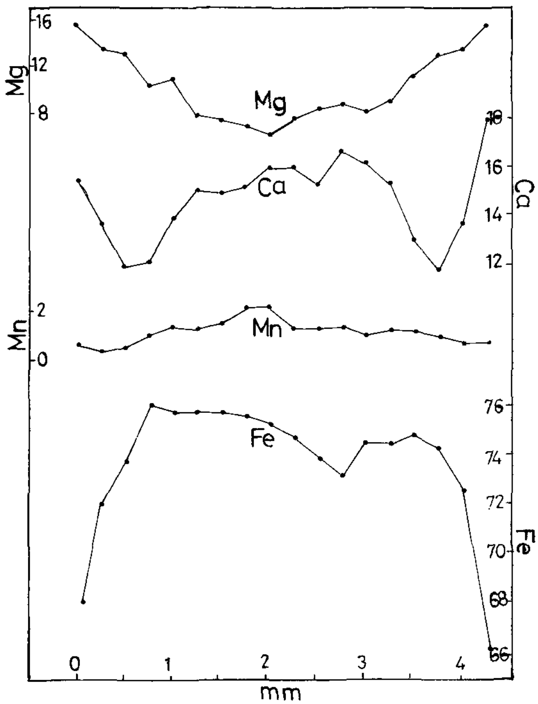
Reactions (10) and (11) involve hydration. Since prograde metamorphism is one of a dehydration, prograde staurolite could not have been produced by reactions (10) and (11). The possibility is, therefore, that staurolite + biotite was produced by a discontinuous reaction:

$$\text{garnet} + \text{chlorite} + \text{muscovite} = \text{staurolite} + \text{biotite} + H_2O \quad (12)$$

With discontinuous reactions, ideally the reactant phases or at least one of them should disappear. This has not happened here probably because these rocks represent a transitional zone between garnet and regular staurolite zone rocks and excess components such as CaO and MnO in garnet and ZnO in staurolite stabilize extra phases.

Garnet profiles in staurolite-bearing rocks (with staurolite either replacing garnet or present in the adjacent matrix) are given in figs. 9 and 10. Unlike 'normal' zoning there is a sudden drop in Fe at the rim. As Fe drops, Ca rises towards the rim (fig. 10). Garnets behave in this way in all staurolite-bearing rocks. Such 'reverse' zoning at the rim has generally been explained by retrogression of garnet to biotite (Grant and Weiblen, 1971) but the garnets in question do not show retrogression but 'prograde replacement' by staurolite. This is because the final layer of garnet which is involved in the discontinuous reaction (12) loses its Fe to staurolite so that there is a strong increase in the Mg/Fe ratio of the outer garnet layer. The appearance of staurolite is thus correlated to the drop in Fe at the garnet rim causing 'reverse' behaviour of Fe at the rim. Since Mn and Ca are antipathetic to Fe in garnets, as Fe drops, Mn (fig. 9) or Ca (fig. 10) increases. Comparison of fig. 9 with fig. 10 suggests that when garnet is resorbed readjustment in either Ca or Mn alone is adequate. In fig. 9 Mn is readjusted while Ca is not. In fig. 10 Ca readjusts but not Mn. Another reason for non-readjustment of Mn in some cases is due to the fact that only the outer layers of garnet are involved in the resorption which are in general too impoverished in Mn to show any significant pattern at the rim.





FIGS. 9 and 10. FIG. 9 (*left*). Compositional profile of a garnet in staurolite-bearing rock in sample 95. Ionic per cent Mg, Ca, Mn, Fe plotted against distance. Mn and Fe show 'reverse' zoning at the rim. FIG. 10 (*right*). Compositional profile of a garnet in staurolite-bearing rock (sample 168). Ionic per cent Fe, Mg, Ca, Mn plotted against the distance. Fe and Ca show 'reverse' zoning at the rim.

The crossing of tie lines of garnets from rocks with and without staurolite, mentioned earlier (fig. 3), is due to the increased Mg/Fe of garnet rims resorbed in the production of staurolite in staurolite-bearing rocks.

Conclusions

The above discussion shows that a number of reactions have contributed to the nature of the garnet zoning. In highly aluminous rocks (suitable to have formed chloritoid) garnet grows at the expense of chloritoid and staurolite, whereas in less aluminous rocks garnet grows at the expense of chlorite. The chemistry of the inclusions in garnet helps to understand the prograde reaction histories in which garnet is involved. Finally, garnet develops 'reverse' zoning at the rim when it is resorbed to produce staurolite.

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REFERENCES

Anderson, D. E. and Buckley, G. R. (1973). *Contrib. Mineral. Petrol.* **40**, 87–104.
Atherton, M. P. (1968). Ibid. **18**, 347–71.
Crawford, M. L. (1977). *Can. Mineral.* **15**, 243–9.
Grant, J. A. and Weiblen, P. W. (1971). *Am. J. Sci.* **270**, 281–96.
Harte, B. and Henley, K. J. (1966). *Nature, London*, **210**, 689–92.
Hollister, L. S. (1966). *Science*, **154**, 1647–51.
Johnson, M. R. W. (1963). *Geologie Mijnb.* **42**, 121–42.
Sivaprakash, C. (1979). Ph.D. thesis, University of Cambridge.
Statham, P. J. (1976). *X-ray Spectrometry*, **5**, 16–28.
Sweatman, T. R. and Long, J. V. P. (1969). *J. Petrol.* **10**, 332–79.
Thompson, A. B. (1976). *Am. J. Sci.* **276**, 401–54.
—— Tracy, R. J., Lyttle, P. T., and Thompson, J. B. (1977). *Am. J. Sci.* **277**, 1152–67.
Tracy, R. J., Robinson, P., and Thompson, A. B. (1976). *Am. Mineral.* **61**, 762–75.
Trzeienski, W. E. (1977). *Can. Mineral.* **15**, 220–56.

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