

## Formation of atoll garnets from the aureole of the Ardara pluton, Co. Donegal, Ireland

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**SUMMARY.** A detailed petrographic and microprobe study was carried out on atoll-shaped garnets from the aureole of the Ardara pluton, in which regionally metamorphosed rocks have been affected by thermal metamorphism. Textural evidence showed that the atoll garnets are formed by replacement mainly by biotite, some plagioclase, quartz, and opaques, and may proceed from the garnet interior towards the margins, or from the margins into the core. Core replacement occurs mainly in those garnets enclosed by quartz or quartz-rich matrix.

Microprobe analyses are presented of garnets in different stages of atoll formation. Compositional profiles at the garnet margins show abnormal (reversed) zoning with increase in MnO and Fe<sub>2</sub>O<sub>3</sub>,<sup>2</sup> marked decrease of CaO, and decrease of MgO towards the extreme edge. With decreasing width of the atoll rims, there is generally an increase in MnO and to a lesser extent Fe<sub>2</sub>O<sub>3</sub>, a decrease in CaO; MgO is variable. The microprobe data support the textural observations and a model for atoll formation involving prograde resorption (i.e. garnet replacement during temperature increase) is presented.

**PREVIOUS** work on atoll garnets has been limited, but selective replacement of the atoll core has been generally considered to be the most likely mechanism of formation in metamorphic rocks (Green, 1915; Williamson, 1935; Rast, 1963, 1965; Forestier and Lasnier, 1969). Such crystal shapes are well known in the field of ore mineralogy (see, for example, Schouten, 1934, 1946; Edwards, 1954), where selective replacement of the crystal core and along rhythmic compositional zones occurs. In contrast Atherton and Edmunds (1966) discounted this mechanism as an explanation for atoll garnets from the Ben Lui schist at Pitlochry. In their view, the microprobe data indicated uniform composition across the garnets, both complete and atoll-shaped, so that selective replacement along rhythmic compositional zones was considered unlikely. Cooper (1972) found no textural evidence for selective replacement of the atoll core in garnets from the Haast area, New Zealand, although chemical zoning exists within the atoll rim and isolated core.

The present contribution sets out data from a detailed microprobe examination of some atoll garnets from a single formation, the Gleengort (Clooney) meta-pelites from the aureole of the Ardara pluton, Co. Donegal (fig. 1), which has been studied previously by Akaad (1956*a, b*) and by Pitcher and Sinha (1957). In this present study thirty-two atoll-shaped garnet crystals were analysed to establish the occurrence of any chemical zoning. This data, together with textural evidence, provides a basis for genetic interpretation.

Garnet analysis were carried out using homogeneous glass standards. Details of

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<sup>2</sup> Total iron as Fe<sub>2</sub>O<sub>3</sub>.

these and the analytical procedures employed are given elsewhere (Smellie, 1972, 1974).

### Petrography

The petrography of the Ardara aureole is well documented (Akaad, 1956*a, b*; Pitcher and Sinha, 1957; Pitcher and Read, 1960; Naggar and Atherton, 1970; and Smellie, 1972 (unpublished thesis), 1974). Thermal metamorphism, which resulted

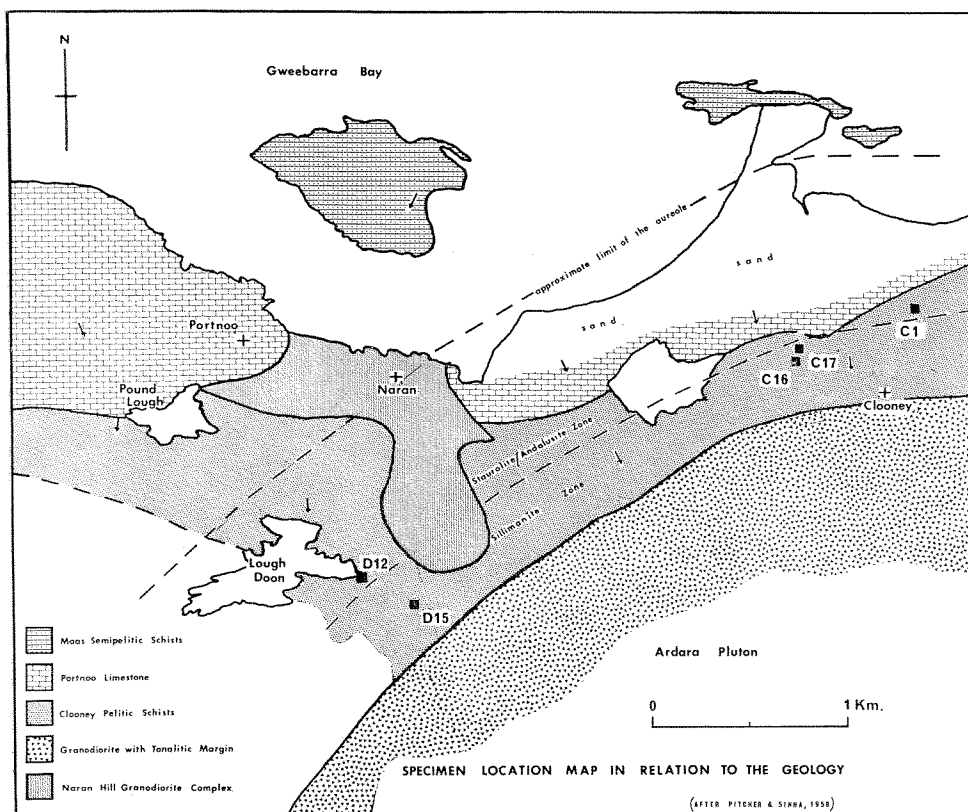


FIG. 1. The north-western part of the aureole, Ardara pluton, Donegal, showing the location of the specimens in relation to the geology. (After Pitcher and Sinha, 1958.)

from the emplacement of the Ardara pluton, was superimposed on pre-existing regional metamorphic rocks dominated by chlorite–garnet–muscovite schists. This produced, in order of decreasing distance from the contact, biotite, garnet, staurolite, andalusite, sillimanite, and cordierite (Akaad, 1956*a, b*). The majority of these thermal garnets show varying degrees of biotite alteration, which form embayments or complete pseudomorphs, but occasionally atoll-shaped garnets result. The occurrence of these atoll-shaped garnets within the aureole do not appear to relate to any specific isograd nor to any strict rock modal values (Table I).

*Specimen C1.* Despite the thermal metamorphism, the dominant pre-thermal regional foliation, distorted by a strain-slip cleavage, can still be traced through the rock and the subsequent porphyroblastic growth of staurolite, plagioclase, and andalusite gives the fabric a pronounced 'augen' character. The euhedral thermal

TABLE I. *Modes of rocks containing analysed garnets*

Specimen No.	C1	D12	C17	C16	D15
Distance from contact	425 m	425	364	310	200
Quartz	29.8	36.3	40.7	44.8	45.0
Plagioclase	—	—	—	—	—
Biotite	20.1	17.8	30.2	45.0	19.4
Muscovite	25.0	26.2	—	—	15.5
Garnet	5.3	7.6	4.9	8.3	8.1
Staurolite	4.8	2.5	1.0	—	—
Andalusite	14.0	8.8	14.5	—	9.5
Sillimanite	—	—	7.7	—	2.2
Opagues	—	—	—	—	—
Apatite	1.0	0.8	1.0	1.9	0.3
Tourmaline	—	—	—	—	—
Total	100.0	100.0	100.0	100.0	100.0

With the exception of Specimen D12, all specimens contain atoll-shaped garnets.

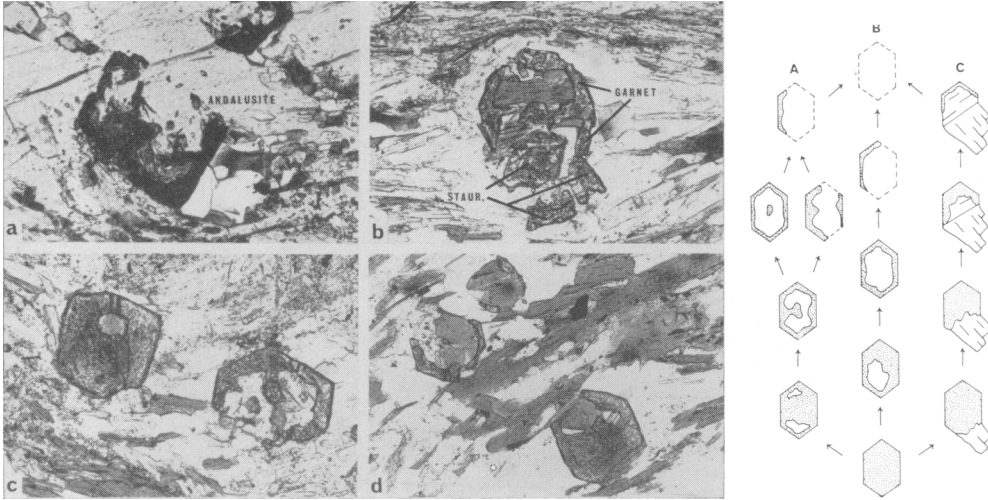
garnets (up to 0.25 mm in diameter) cross-cut the pre-thermal foliation and are commonly included by plagioclase, andalusite, and, in isolated areas, staurolite (up to 0.7 mm in length). Breakdown of garnet occurred before the completion of staurolite and andalusite so that these phases may partly replace both the biotite embayments and pseudomorphs after garnet (fig. 2 *a, b*). The fact that staurolite and andalusite are higher-temperature minerals in the aureole than garnet, and yet in some cases occupy the atoll cores, clearly shows the prograde nature of the garnet breakdown. There is no textural or microprobe evidence that garnet may have occurred later than staurolite or andalusite.

Nearly all the garnets in the specimen show some degree of breakdown with replacement by biotite, small amounts of quartz, plagioclase, and in a few cases opaques. About 90 % of the garnets show atoll characteristics at various stages of formation and the remainder are either almost complete, or with large biotite embayments, or mere fragments within the biotite pseudomorphs (fig. 3).

Garnet instability and subsequent breakdown is probably a result of reactions at higher temperatures involving andalusite and staurolite formation, and is prevalent in rocks that contain andalusite but lack staurolite or vice versa. Texturally andalusite occurs within biotite pseudomorphs after garnet and also within and around atoll garnets (fig. 2*a*). This would tend to support the following reaction having taken place on a local scale: garnet + muscovite  $\rightarrow$  andalusite + biotite + quartz. Most of the andalusite, however, has resulted from the pre-thermal fabric: muscovite + chlorite  $\rightarrow$  andalusite + biotite + quartz + H<sub>2</sub>O. There are many examples of large andalusite

crystals that have included euhedral garnets with no evidence of reaction around the garnet edges.

Staurolite nucleation has probably had the same effect on the stability of garnet, and in many cases can be observed in close association with biotite within or near partly replaced garnets (fig. 2b). In the majority of cases, however, there is no andalusite



FIGS. 2 and 3: FIG. 2 (left). *a.* Andalusite enclosing and penetrating an atoll-shaped garnet (black). Specimen C1; crossed nicols;  $\times 25$  diameters. *b.* Staurolite growth within an atoll garnet. Note also the preservation of the garnet core almost completely isolated from the rim. Specimen C1; plane polarized light;  $\times 25$  diameters. *c.* Contrasting stages of atoll formation with preservation of the atoll core in the more advanced stage. Specimen C1; plane polarized light;  $\times 20$  diameters. *d.* Successive stages of atoll formation are shown from bottom to top of photomicrograph. Note the euhedral interfaces with quartz and feldspar and the final atoll stage in which a biotite pseudomorph has almost completely replaced the garnet. Specimen C1; plane polarized light;  $\times 6$  diameters. FIG. 3 (right). Idealized diagram illustrating the three main atoll-forming trends in Ardara. The garnet is speckled.

or staurolite involved directly with the replaced garnets. Garnet margins that have been breached are usually in close association with muscovite-rich foliation bands. Within these bands, surrounding the breach in the garnet, is a biotite-rich area, which suggests the possibility of a reaction between garnet and muscovite to form biotite and some recrystallized K-deficient muscovite. This may be substantiated by, in some cases, the presence of small muscovite blades, together with biotite, within the atoll garnets. The reaction probably nucleated at a highly reactive point within or at the margin of the garnet and gradually eroded the core. The rims, and occasionally projections of the garnet from the rims into the core, remained stable during much of this replacement process, although ultimately they too may be replaced by biotite with formation of, in many cases, a euhedral biotite pseudomorph. In a few instances the core is apparently (as seen in two dimensions) isolated from the rims and may be among the last fragments to disappear (fig. 3A). In several examples dissolution begins

at the crystal edge, the biotite becoming increasingly embayed into the garnet until only rim fragments remain (fig. 3C). In the majority of cases where the crystal rims or edges are in contact with quartz or feldspar there is a sharp outline. This probably indicates that little alteration at this crystal edge has occurred, in contrast with the biotite contacts where the garnet rims and edges are invariably embayed, breached, or totally replaced.



FIGS. 4 and 5: FIG. 4 (left). *a.* Atoll garnet showing complete replacement of the core by biotite and opaques. Note the preservation of the rims in contact with quartz/feldspar. Specimen C1; plane polarized light;  $\times 16$  diameters. *b.* Atoll garnet showing replacement of core by biotite, quartz, and a little plagioclase. Mottled texture surrounding the atoll and penetrating the bottom rim is sericite after andalusite. Specimen D15; crossed nicols;  $\times 16$  diameters. *c.* Atoll garnet showing almost complete isolation of core from the rim by selective replacement of the garnet by quartz and biotite. Specimen C17; plane polarized light;  $\times 25$  diameters. *d.* Complete and atoll garnets with biotite and some opaques replacing the atoll core. Specimen D15; plane polarized light;  $\times 16$  diameters. FIG. 5 (right). Microprobe traverse across an almost intact thermal garnet from Ar dara. Stippled areas represent biotite and the scale bar is  $100 \mu\text{m}$ . Specimen D12.

The rims, and in some instances the cores, are usually the last to disappear. This suggests that either the initial zoning characteristics enable these parts of the crystal to remain relatively stable, or there is a redistribution of elements within these areas rendering them more stable. There appears to be no microscopic evidence to explain why these garnets, in contrast to the majority of garnets in the aureole, should break down so completely in such a manner.

The only other specimens that contain adequate occurrences of atoll garnets are C17 and D15 (fig. 4 b, c, and d), and the textural observations described above typify atoll formation for these examples also. It is noticeable in specimen C17, however, that in most garnets a breached rim or a small remnant core remain (fig. 4c).

*Analytical results: Specimen D12*

Fig. 5 illustrates typical compositional profiles across relatively intact Ardara garnets found in the outer aureole, common in location to the atoll garnets described in this paper. The analyses indicate trends similar to those found in many other thermal and regionally metamorphosed areas (see, for example, Hollister, 1966, 1969;

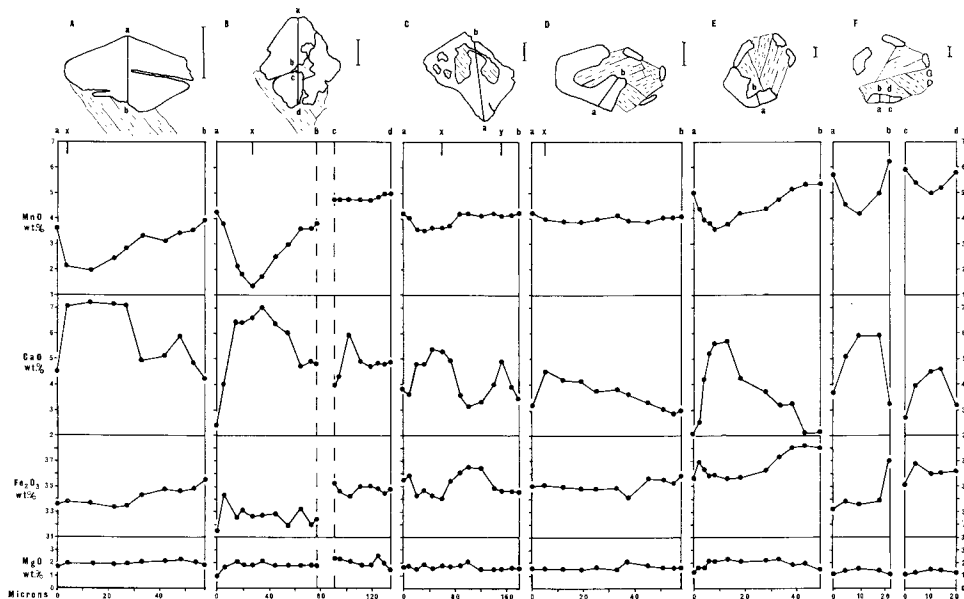


FIG. 6. Microprobe traverse across thermal garnets in various stages of atoll formation. Scale bar is 40  $\mu\text{m}$ . Specimen C1.

Atherton, 1968) and indicate that these Ardara garnets initially grew according to the Rayleigh Fractionation Model (Hollister, 1966). Small marginal discrepancies, however, do occur, and these are more obvious at the garnet/biotite interface than at the garnet/quartz interface. Such marginal discrepancies indicate reversed zoning in which MnO increases towards the garnet edges; CaO decreases antipathetically;  $\text{Fe}_2\text{O}_3$  decreases sharply at the quartz interface but levels out at the biotite interface; MgO shows small decreases. Reversed zoning is common to most garnets in the Ardara aureole, particularly marked at the garnet/biotite interfaces (Smellie, 1972, unpublished thesis).

*Specimen C1*

This specimen was selected as showing garnets ranging from almost complete to atoll rim fragments, and a total of twenty-four traverses were analysed across thirteen garnets. Seven such traverses across six garnets are shown in fig. 6, illustrating a decrease in atoll rim width from D to F.

*Garnet A.* Apart from some alteration to biotite along one edge, this garnet is

almost complete. Traverse *a b* is taken from the garnet/quartz interface at *a* to the altered-garnet/biotite interface at *b*. The MnO distribution shows an increase towards the garnet centre from just within the garnet/quartz interface at *x*. This increase from 2.1 % to 3.4 % represents a preserved remnant of the original garnet compositional zoning before garnet breakdown (compare D12 in fig. 5 allowing for the cut-effect). This is supported by the fairly uniform CaO profile (approx. 7.0 %) and the decrease of Fe<sub>2</sub>O<sub>3</sub>; MgO is uniform. These original trends, so obvious in specimen D12, have in this case become even more distorted by the reversed zoning of the outer 5 μm at *a* and from the centre of the garnet to the biotite interface at *b*. Such marginal variations are similar to those described for specimen D12. The approximate uniformity of edge values at *a* and *b* for, in particular, CaO, MnO, and MgO indicate that the mechanism producing such marginal variations may be occurring under conditions of equilibrium. This, however, is not reflected by Fe<sub>2</sub>O<sub>3</sub>.

*Garnet B.* The core shows partial alteration, mainly to biotite, with marked alteration to biotite along the garnet edge at *d*. Similar compositional trends to garnet A are apparent with the original zoning preserved from *x* to *b* but not along *cd* where the marginal influence is dominant. The variation of edge values *a*, *b*, *c*, and *d* indicate disequilibrium. The higher values of MnO and Fe<sub>2</sub>O<sub>3</sub> and the lower values of CaO at *c* and *d* reflect the fact that alteration to biotite occurred mainly at these edges with a little at *b*. Edge *a* failed to equilibrate to comparable values.

*Garnet C.* Garnet alteration to biotite is restricted to within the garnet margins; the external garnet edges are in contact with quartz or a quartz-rich groundmass. Along traverses *a b* the effects of alteration extend from *x* to *y*. Such effects are an increase of MnO from 3.6 to 4.1 % and Fe<sub>2</sub>O<sub>3</sub> from 34.0 to 36.5 %; CaO decreases from 5.3 to 3.1 %, and a small decrease of MgO (approx. 0.3 %) also occurs.

*Garnet D.* Replacement is more complete with the remnant garnet existing as a discontinuous rim indicating the original outline. Replacement by biotite has either proceeded from within the garnet, similarly to garnet C, or inwards from a breach in the margin, towards the apparently stable garnet/quartz interface at *a*. Such a process is evident from the compositional profiles, which show, in particular, a decrease of CaO towards *b* and a maximum at *x*. In the Ardara garnets, a decrease in CaO is the most sensitive indicator to garnet breakdown mainly because it is removed during garnet replacement, becoming accommodated in the recrystallizing plagioclase that commonly exists within the complete and partial pseudomorphs of garnet. Another example is in garnet A, where the resorbed edge at *b* can be traced midway into the garnet due to the CaO reduction. Further evidence in garnet D is the Fe<sub>2</sub>O<sub>3</sub> increase towards *b*; MnO and MgO, however, are fairly uniform. With the exception of Fe<sub>2</sub>O<sub>3</sub> the remaining oxides each show comparable edge values, which indicates a possible approach to equilibrium during replacement.

*Garnet E.* Along traverse *a b* a similar CaO distribution to that of garnet D is obtained. In this case the asymmetry of the MnO and Fe<sub>2</sub>O<sub>3</sub> profiles, both showing a marked increase especially towards the garnet/biotite edge, and the MgO decrease all support the textural evidence that garnet alteration occurred from the centre towards the rims.

*Garnet F.* Both traverses *ab* and *cd* show that the distributions of MnO, CaO, and MgO are symmetrical and Fe<sub>2</sub>O<sub>3</sub> asymmetrical across the atoll rim. The variation in edge values of, in particular, Fe<sub>2</sub>O<sub>3</sub> and MnO over such a small length of atoll rim (20 μm) indicates disequilibrium.

The results given in fig. 6 show that an over-all increase in MnO occurs with decrease in width of the atoll rim (i.e. from A to F). With the exception of garnets E and F an antipathetic decrease of CaO is also indicated. The anomalous results in E and F are probably due to a reaction of limited extent occurring at the garnet/quartz interface (indicated by a very narrow breadth of MnO increase and CaO decrease) combined with the possible slowing down of the reaction at the garnet/biotite interface as the rim becomes narrower.

#### *Specimen D15*

Several garnets were analysed; one almost complete crystal and another atoll structure are shown in fig. 7.

*Garnet A.* Traverse *ab* shows a similarity of marginal profiles to those of specimens D12 and C1. Because of the greater garnet size (approx. 0.5 mm in diameter) than those described in specimen C1, most of the garnet is free of the marginal variation so that more of the original zoning is preserved. This reflects the normal trends towards the garnet centre (*x-y*); increase in MnO and CaO with an antipathetic MgO and Fe<sub>2</sub>O<sub>3</sub> decrease. The discrepancy of edge values between the garnet/biotite and garnet/quartz interfaces indicate a lack of equilibrium or diffusion difficulties.

*Garnet B.* Traverse *cd* shows similar trends to specimen C1. MnO and CaO profiles are more uniform since this garnet is much nearer the igneous contact (200 m) so that equilibration across the atoll rim is more complete. The marginal zone next to the garnet/quartz interface is again narrower than that of the garnet/biotite interface. Comparison of compositional values between the centres of the atoll rim and the adjacent complete garnet show that with atoll formation there is an increase in MnO and MgO and a decrease in CaO; Fe<sub>2</sub>O<sub>3</sub> appears relatively unchanged. This is in general agreement with specimen C1.

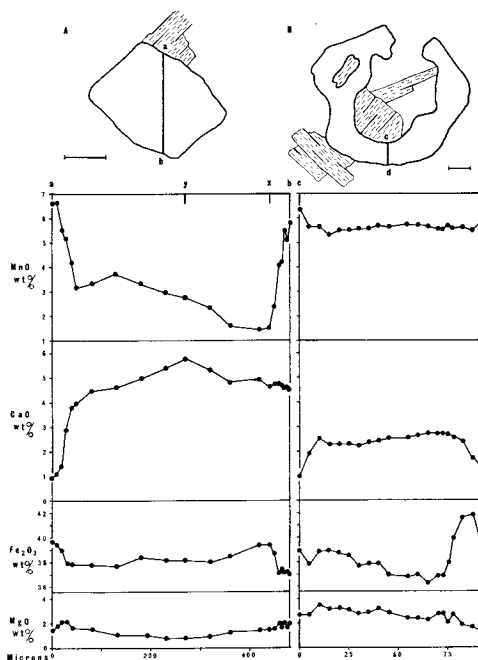


FIG. 7. Microprobe traverses across a complete garnet (*ab*) and adjacent atoll (*cd*). Scale bar is 200 μm for garnet A and 100 μm for garnet B. Specimen D15.



*Genesis*

The analytical data for specimens D12, C1, and D15 show that before replacement the garnets were normally zoned according to the Rayleigh Fractionation Model. Subsequent instability and replacement of the garnets occurred in two main ways: by preferential resorption of the core, or by dissolution of parts of the garnet exterior.

In the examples known to the writer, preferential replacement of the core tends to occur only where the garnet was surrounded by a quartz or quartz-rich matrix. This is because garnet/quartz interfaces are thermodynamically much more stable under metamorphic conditions than garnet/mica interfaces. This hypothesis is supported by the fact that garnet forming in a quartz-rich matrix tends to grow by extending along quartz/quartz interfaces, often in the form of very thin dendrite-like arms. Such a low dihedral angle shows that the garnet/quartz interfacial energy is low (Smith, 1952), and the interface would thus be less reactive than a mica/garnet interface. In such cases, therefore, reaction resulting in replacement would tend to be nucleated at points or surfaces of lattice disconformity or distortion, such as cracks on any scale, or even highly stressed zones that resulted in the development of high dislocation density.

Nucleation would therefore occur where one of these cracks or stressed zones met the surface, but reaction would quickly move inwards along the grain boundary. Hence it is possible that when the reaction reached a compositional zone that was sufficiently out of equilibrium with the stable growing biotite, nucleated in a MnO-poor environment (the garnet edge), it quickly spread along this compositional zone boundary (probably also a crystallographic boundary).

If the original compositional zoning were rhythmic, a discrete zone or zones would be preferentially replaced, leaving the rest of the crystal intact. This simple model is probably complicated by other factors such as small and perhaps randomly distributed volumes of high lattice distortion. These might quickly be replaced preferentially, regardless of the composition of their volume, with the formation of irregularly distributed replacement areas.

The replacement process could be inhibited or prevented in any one place, at any stage in the development, by localized sealing of diffusion channels and consequent shortage of the large hydroxyl groups and potassium ions necessary for biotite formation.

Resorption of the external garnet edges occurs within the micaceous bands. Textural evidence shows that it begins at the garnet margin in the presence of muscovite, which is generally near or bordering the crystal edges. Resorption continues until an atoll rim remains, usually bordered by quartz. In cases where the garnet breaks down within an entirely micaceous band, it is apparently replaced from the boundary inwards, eventually forming a biotite pseudomorph, with one or two rounded fragments of garnet remaining. The reason why so few atoll garnets exist wholly within micaceous bands is uncertain, although the muscovite-rich assemblage surrounding the garnet would tend to be conducive to the initiation of replacement reactions at various points of weakness around the garnet margins. Generally, however, only the

crystal face nearest to the micaceous band begins to break down; the remaining crystal faces are normally bordered by quartz.

Replacement of the garnets by the above means results in the unusual compositional profiles at the margins of the almost complete and atoll garnets, such profiles being a common feature in the majority of garnets in the Ardara aureole. Previous models for such an increase of MnO and Fe<sub>2</sub>O<sub>3</sub> and decrease of MgO and CaO at the garnet edge have involved retrograde regional metamorphism (Grant and Weiblen, 1971), rapid thermal growth (Edmunds and Atherton, 1971), or continuous garnet growth with falling temperature (Kurat and Scharbert, 1972). None of these models, however, satisfactorily explains the similar compositional variations in Ardara. The most convincing evidence that indicates an alternative model is provided by the textural relationships described above. In particular, staurolite and andalusite replace the biotite-rich embayments and cores of thermally produced garnets. As staurolite and andalusite in the Ardara aureole are higher temperature minerals than garnet, it seems probable that partial garnet breakdown had occurred prior to, or contemporaneous with, staurolite/andalusite growth and was therefore more likely to be due to prograde thermal rather than retrograde metamorphism, unless complex temperature fluctuations for which there is no other evidence occurred in the aureole. This is supported by microprobe data for garnets completely and partially enclosed by staurolite and andalusite, which indicated no obvious interaction between garnet and the later staurolite growth (Smellie, 1972 (unpublished thesis), 1974). Garnet breakdown and replacement therefore had probably been completed before staurolite growth had enclosed the garnet remnants, further indicating the prograde nature of the garnet breakdown.

Prograde resorption of garnet meant that MgO, CaO, and Fe<sub>2</sub>O<sub>3</sub> were removed from the garnet to contribute to the formation of biotite and plagioclase, the latter recrystallizing with increasing temperature, possibly becoming richer in CaO (*cf.* Engel and Engel, 1960). Because MnO is not necessary for biotite and plagioclase formation and is particularly suitable for the garnet structure, it is retained preferentially along with some Fe<sub>2</sub>O<sub>3</sub> at the resorbing edge of the garnet. In contrast, the demand for MgO and CaO results in a decrease at the garnet edge. The marginal variations will therefore generally involve an increase in MnO, a less marked Fe<sub>2</sub>O<sub>3</sub> increase, and a decrease of CaO and MgO. As resorption continues to the point of atoll formation therefore, the atoll rims become richer in MnO and possibly Fe<sub>2</sub>O<sub>3</sub>, and less rich in CaO with decreasing width.

In an attempt to re-equilibrate, the edges of the garnet away from the site of biotite growth may undergo compositional readjustment depending on the availability of ions and the ease of diffusion. This results in the unreplaced margins usually achieving similar compositional levels to the resorbing edges, but these marginal zones are much narrower and more prone to variation than the reacting edges. This indicates that equilibrium had not been achieved completely and that diffusion was very localized giving rise to variation of edge values recorded in many instances described above.

*Acknowledgements.* I am especially indebted to Dr. K. A. Jones (Belfast) for many stimulating discussions and his helpful criticism, which improved the manuscript. Thanks are due to

Dr. R. A. Bowes (Glasgow), in particular, and Dr. D. Field (Nottingham) for their critical reading of the manuscript and Mr. D. Jones (Nottingham) for photography.

This paper forms part of a major study carried out at the Queen's University of Belfast during the tenure of a Post-graduate Studentship from the Ministry of Education, Northern Ireland, which is gratefully acknowledged.

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[Manuscript received 14 January 1974; revised 9 May 1974]