ZONED AND UNZONED GARNETS FROM THE GRENVILLE GNEISSES AROUND GANANOQUE, ONTARIO

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ABSTRACT

Strict limitations are placed on reacting chemical systems during metamorphism if one or more of the mineral phases is compositionally zoned. An investigation of the volumes of equilibrium in some high-grade metamorphic rocks from the Grenville of southeastern Ontario, therefore, included a study of possible zoning of the garnets.

Traverses at 25 micron steps across four garnets, employing a laser-excited spectrochemical technique, revealed no compositional zoning with respect to Fe, Mg, Mn or Ca in three of the grains. High Mn values, however, occur in the central portion of one garnet within an area of quartz inclusions. It is proposed that the garnets of these rocks were originally zoned and that later metamorphic events have eliminated this zoning in most of the garnets, some still showing a relic zoning in their central portions.

INTRODUCTION

During a study of the spatial extent of chemical equilibration in some high-grade metamorphic gneisses from the Grenville Series of the Gananoque area, Ontario (Blackburn, 1968), *in situ* determinations for Fe, Mg, Mn and Ca were made using laser-excited spectrochemical techniques. In this manner, it was possible to delimit zones, on the order of a few centimeters, which contained garnets of the same composition with respect to a particular element. This in turn outlined particular domains or volumes of equilibration between garnet and surroundings with respect to that element. However, if the garnets of these gneisses are zoned, much of the variation observed was probably due to poor precision of the point of analysis on each garnet.

A recent discussion of zoning in garnets by Hollister (1966) points out the problems of equilibration studies if one or more of the minerals present is observed to be compositionally zoned. Hollister finds that compositional variations in zoned garnets follows a Rayleigh fractionation model (Rayleigh, 1902) where only the extreme outermost layer of the garnet is part of the reacting system at any one stage of garnet growth. The garnets from the schists of the Kwoiek area of British Columbia (Hollister, 1966) and those described from kyanite-zone schists from central Vermont (Albee *et al.*, 1966) show a strong systematic variation of Mn decreasing outwards from the grain centre with concomitant Fe and Mg variation.

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Thus, in the present work, it was imperative to inspect the garnets of the gneisses studied for possible compositional zoning. If the garnets are zoned and care was not taken to make all analyses at the outermost layer of each garnet, observation of the garnet-garnet or garnet-rock reaction system would not be possible.

Description of the Samples

The samples selected for the study of spatial degree of equilibration included a strongly foliated biotite-garnet-cordierite gneiss (No. 17) and a pyroxene-garnet gneiss (No. 42) with a less distinct foliation. Modal analyses for these rocks are given in Table 1.

Table 1. Modal Analyses of the Gneisses Selected for Investigation of Garnet Zoning

	17	42	8
Quartz	34.1	17.8	7.3
K-Feldspar	22.9	56.9	16.3
Plagioclase	2.9	9.7	48.7
Biotite	3.5	1.4	12.6
Garnet	11.1	5.2	4.8
Sillimanite	9.9	—	—
Opaques*	2.2	1.7	5.2
Cordierite	13.4	—	1.8
Zircon	Tr	—	Tr
Spinel	—	—	0.8
Chlorite†	Tr	0.3	1.1
Muscovite	—	—	0.8
Hypersthene	—	6.9	—

*Magnetite, ilmenite and pyrite.
†Mainly as alteration of cordierite.

Sample 17 is a medium-grained, highly foliated gneiss with quartz, K-feldspar, garnet, biotite and cordierite as major component minerals. Microscopically, the rock exhibits an extremely well-developed foliation with foliation planes populated for the most part with biotite, sillimanite, garnet and cordierite grains. A section perpendicular to the foliation exhibits severely elongated garnets in the foliation plane. Some of these elongated garnets contain sillimanite needles which continue uninterrupted through the garnet. The elongated garnets also have local inclusions of quartz, K-feldspar and biotite; the biotite inclusions, like those of sillimanite, retain their orientation with respect to foliation and lineation. The elongated garnets are mantled with cordierite and K-feldspar.

Sample 42 exhibits a well developed layering in outcrop but foliation is not distinct in hand specimen due to the lack of platy and elongate minerals. The major phase constituents are quartz, K-feldspar, plagioclase, orthopyroxene and garnet. Garnet occurs as small rounded grains with sparse inclusions of quartz. Biotite is a minor constituent of the rock and occurs as small ragged, unaltered grains scattered throughout the gneiss but concentrated in pyroxene-garnet-biotite layers.

Altogether, four garnets were examined for compositional zoning. Two of these garnets were from sample 17 and showed minor inclusions of sillimanite. One garnet was from sample 42 where inclusions in the garnets were rare and the last was from sample 8 and contained quartz inclusions located in a clump in the centre of the garnet grain.

Sample 8 is a coarse grained quartz-feldspar-garnet-biotite gneiss with well-developed foliation. Garnet occurs as small rounded and elongated grains which are generally free of inclusions. The garnet is in close association with cordierite, magnetite and green spinel. The modal analysis of sample 8 is given in Table 1.

Analytic Technique

Compositional variations in the garnets were investigated with the use of a Mark II Laser Microprobe at the Jarrell-Ash Company in Waltham, Massachusetts. The Mark II is the latest model of the laser microprobe and features a non-temperature sensitive neodymium laser with controlled output energy and an optical system much improved over earlier models. A detailed description of laser-excited spectrochemical analysis of silicates is given elsewhere (Blackburn, Pelletier & Dennen, 1968) and will not be discussed here. Operating parameters used in the zoning investigation are given in Table 2.

Table 2. Operating Parameters Used in the Investigation of Zoning in the Garnets

Source:	Jarrell-Ash Co. Mark II Laser Microprobe.
Spectrograph:	1 m Czerny-Turner mounted spectrograph. Jarrell-Ash Co.
Electrodes:	1/8th inch National Carbon Co. AGKSP graphite rods, pointed pencil sharp.
Photographic Plates:	Eastman Kodak Type 103-0.
Analytic Gap:	2 mm
Cross Excitation Voltage:	2000 volts.
Wave Length Region:	2600 Å–4200 Å.
Plate Development:	4 minutes at 20°C in Kodak D-19 developer.

The four garnets were traversed at approximately 25 micron intervals and intensity ratios attained by microphotometry. Conversion of these intensity ratios to concentration ratios was made possible by comparison with chemically analyzed standards.

Results

Figure 1 shows the Mn/Fe + Mg + Mn profile across a garnet exposed on Section 17-I which is cut perpendicular to the foliation. The traverse is in the short axis direction of one of the garnets which is elongated and flattened in the plane of foliation. As is evident from Fig. 1A, no zoning with respect to manganese is apparent within the limits of analytic error. Further, there was no zoning of the garnet with respect to Fe and Mg.

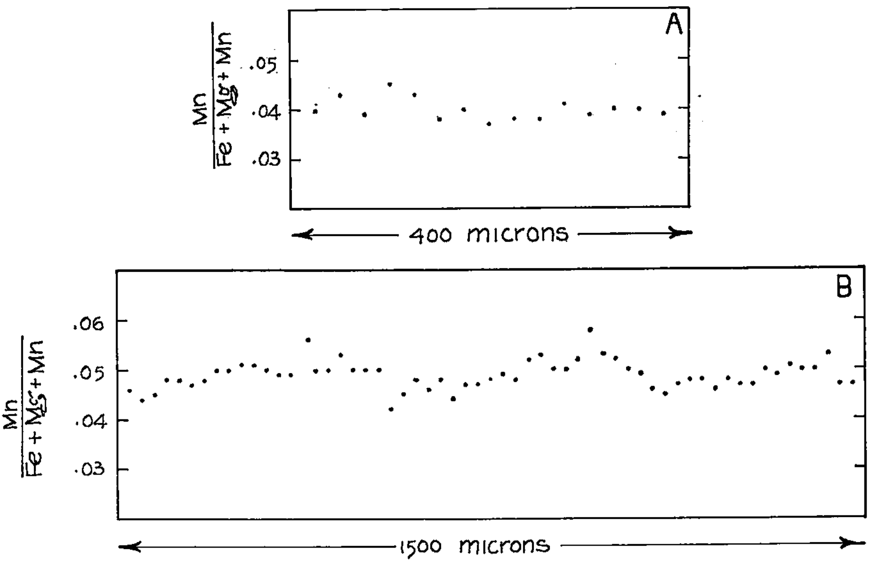


FIG. 1. A. Mn profile across a garnet from Sample 17 cut perpendicular to the foliation. B. Mn profile across a garnet from Sample 17 cut parallel to the foliation.

A traverse across a garnet of Sample 17 cut parallel to the foliation (section 17-II) showed no compositional zoning with respect to Mn, Fe or Mg. The profile of the compositional ratio Mn/Fe + Mg + Mn in this grain is shown in Fig. 1B. The profile shows a semblance of an oscillatory zoning with respect to Mn. However, this variation is within the limits of analytic error.

Figure 2A illustrates the Mn profile across a garnet from section 42-II cut parallel to the foliation. No significant inhomogeneity is noted. The traverse across this grain found it homogeneous with respect to Fe and Mg as well.

The only zoning observed was along a traverse across a garnet from sample 8 (Fig. 2B) which showed a distinct rise in the ratio Mn/Fe + Mg + Mn from about 0.020 at the edges to 0.070 near the centre. The area in which the high Mn values are located corresponds exactly with

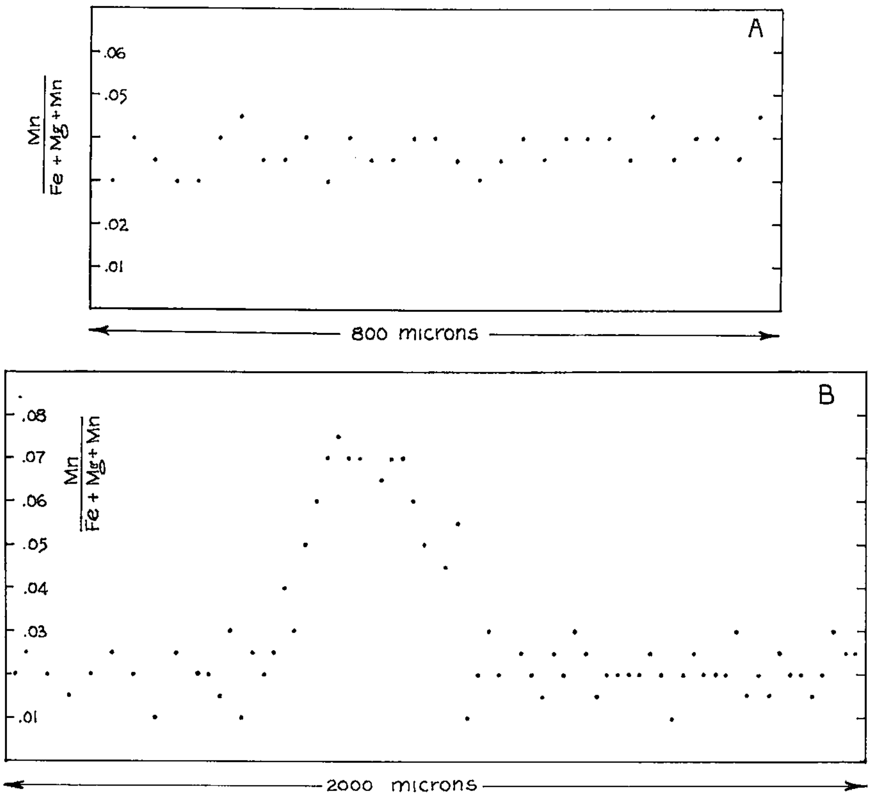


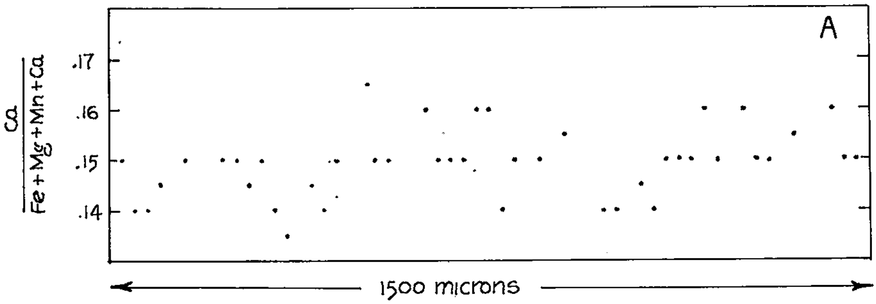
FIG. 2. A. Mn profile across a garnet from Sample 42 cut parallel to the foliation. B. Mn profile across a garnet from Sample 8 cut oblique to the foliation. High Mn values in centre of grain coincide with a clump of quartz inclusions.

the clump of small quartz inclusions. No inclusions were observed in the outer regions of the grain where constant low atomic ratios for Mn prevail.

Hollister (1966) has mentioned the possibility of calcium zoning within garnets. This possibility was investigated along with Mn, Fe and Mg and no compositional zoning with respect to Ca was observed. Figures 3A and 3B show Ca profiles across Sections 17-II and 17-I respectively. All variations are within the standard deviation of analysis.

Thus it is concluded that the compositional zoning of garnets in these rocks is not prevalent and that the variations of garnet compositions within a hand specimen are real. Other factors which lead to this same conclusion are:

1. No optical zoning was evident in any garnets examined.
2. During replicate analyses of the garnets in matrix, no care was taken to "shoot" the same garnet in the same place each time. This had



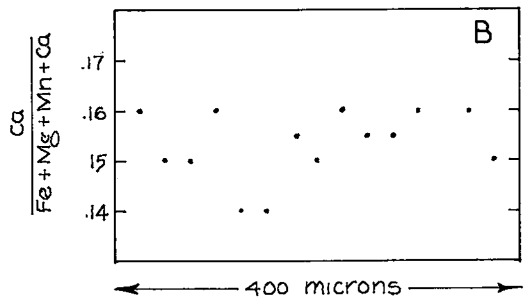


FIG. 3. A. Ca profile across a garnet in Sample 17 cut parallel to the foliation. B. Ca profile across a garnet in Sample 17 cut perpendicular to the foliation.

no effect on the precision of the determinations for the various elements within a single grain.

3. If the garnets of specimen 17-I and 17-II had been zoned, spatial equilibration domains as found (Blackburn, 1968) would not have been observed as the determinations were not made on the edge of each grain, i.e., within the reacting thermodynamic system.

Discussion

Zoning, or the lack of it, in minerals is a reflection of the velocity of growth since zoning implies that the internal equilibration of the minerals has not had time to take place. Rast (1965) suggests that the presence of inclusions in minerals of metamorphic rocks represents a higher velocity of growth, and that this higher velocity of growth reflects the chemical state of the immediate neighbourhood of the point of mineral nucleation. Sturt & Harris (1961) cite an example of replacement of amphibole by garnet where the quartz, interstitial to the garnet, remains unaffected. This may also be the case in many of the elongated garnets of specimen 17 where local inclusions of sillimanite continue uninterrupted through the garnet along the foliation surface. Although zoning is not evident at present in the garnets of this study, the unusual clumping of quartz inclusions in the garnet from sample 8 coupled with the higher Mn values of the garnet in the region of this clumping suggests that the garnets of these gneisses did indeed grow quickly and were at one time zoned, at least with respect to Mn. It is proposed that the garnets have later equilibrated internally expelling non-stoichiometric included material and thus eliminated compositional zoning.

The formation of metamorphic minerals in internal equilibrium is dependent on a sufficient reaction time for the minerals to nucleate and grow maintaining internal as well as external equilibrium. However, Buddington (1965) suggests that temperatures above the garnet equilibrium temperature will be required to facilitate reaction. It is thus possible that zoned garnets have grown quickly under temperature conditions higher than that needed for garnet production. A subsequent rapid decline in temperature would leave garnets with only their extreme edges in the reaction system. This is possibly the case in the Kwoiek area of British Columbia (Hollister, 1966) and the Lincoln Mountain Quadrangle, Vermont occurrence (Albee, *et al.*, 1966). However, if temperatures levelled off for an extended period of time, or if there was a later metamorphic event with temperatures near the almandine stability region, redistribution of stoichiometric and non-stoichiometric material within the garnet might take place, as in specimens 17 and 42, or in part, as in specimen 8.

The gneisses selected for this study are typical of those in the Grenville structural province of southeastern Ontario. The description of geologic setting of this area and its metamorphic history (Wynne-Edwards, 1959, 1962, 1967) suggests deep-seated regional metamorphism with superimposed contact metamorphic effects during the intrusion of conformable granitic rocks. Geochronologic studies by Krogh (1964, 1966) support the idea of polymetamorphism in this area. The above scheme for the formation of zoning and its later destruction is entirely possible.

It should be noted here that the nucleation and growth of a zoned phase need only involve equilibration of that phase, at any particular instant, with its immediate surroundings. That is, mosaic or local equilibration may take place on a very small scale, possibly only between adjacent mineral phases. Equilibration volumes on a larger scale, such as found in these gneisses (Blackburn, 1968), which range up to several centimeters in one axial direction would necessarily involve chemical communication among the garnets within those volumes producing garnets of similar compositions. Although, the growth rate of metamorphic minerals may be a constant for a particular set of conditions, the process of nucleation need not be instantaneous for all garnets (Kretz, 1966). Thus the zoning pattern for all garnets within a particular gneiss need not be the same.

Equilibration of garnets over a volume involving several garnet grains necessitates the internal re-equilibration of each garnet and the redistribution of components among those garnets thereby destroying any zoning formed during growth.

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References

Albee, A. L., Chodos, A. A., & Hollister, L. S. (1966): Equilibration volumes for different species in three assemblages of Kyanite-zone schists, Lincoln Mountain, Vermont (Abstract), *A.G.U. Trans.*, **47**, 213.

Blackburn, W. H. (1968): The spatial extent of chemical equilibrium in some high-grade metamorphic rocks from the Grenville of southeastern Ontario, *Contr. Mineral and Petrol.*, **19**, 72.

——— Pelletier, Y. J. A., & Dennen, W. H. (1968): Spectrochemical determinations in garnets using a laser microprobe: *App. Spectro.*, **22**, 278.

Buddington, A. F. (1965): The origin of three garnet isograds in Adirondack gneisses *Min. Mag.*, **34**, 71–81.

Hollister, L. S. (1966): Garnet zoning: an interpretation based in the Rayleigh fractionation model, *Science*, 1646–1651.

Kretz, Ralph (1966): Grain size distribution for certain metamorphic minerals in relation to nucleation and growth, *J. Geol.*, **74**, 147–174.

Krogh, T. E. (1964): Strontium isotope variation and whole rock isochron studies in the Grenville Province of Ontario, *Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass.*

——— (1966): Whole rock Rb-Sr studies in the northwest Grenville area of Ontario, *A.G.U. Trans.*, **47**, 208.

Rast, Nicholas (1965): Nucleation and growth of minerals, in *Controls of Metamorphism*, W. S. Pitcher and G. W. Flinn, editors, John Wiley and Sons, Inc., N.Y.

Rayleigh, L. (1902): *Phil. Mag.* (*6th series*), **4**, 521.

Sturt, B. A., & Harris, A. L. (1961): The metamorphic history of the Loch Tummel area, Central Perthshire, Scotland, *Liverpool-Manchester Geological J.* **2**, 689.

Wynne-Edwards, H. R. (1959): Westport map-area, *Geol. Surv. Canada, Map 28-1959.*

——— (1962): Gananoque map-area, *Geol. Surv. Canada, Map 27-1962.*

——— (1967): Westport map-area, Ontario, with emphasis on the Precambrian rocks, *Geol. Surv. Canada Mem.* **346.**

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