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A MINERALOGICALLY AND CHEMICALLY ZONED GRANULITE-FACIES COTICULE FROM THE LOWER SILURIAN RANGELEY FORMATION, SOUTH-CENTRAL MASSACHUSETTS

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ABSTRACT

A distinctive spessartine garnet–quartz-rich pod or coticule (14 × 12 × 11 cm) in granulite-facies pelitic schist of the Silurian Rangeley Formation in south-central Massachusetts has been investigated to determine its protolith and understand its geochemistry and mineralogical evolution. The pod is symmetrically layered on both a macroscopic and microscopic scale. A rim-to-core zoning is observed: (1) host pelitic schist composed of Qtz – Pl – Kfs – Grt($\mathrm{Alm_{60-63}Prp_{26-27}Sps_{8-10}Grs_4}$) – Bt – Sil ± Ilm ± Po ± Ap; (2) a quartzofeldspathic layer 0.5 – 2.5 cm thick composed of Qtz – Kfs – Pl – Grt($\mathrm{Alm_{58-60}Prp_{27}Sps_{10-11}Grs_4}$) – Rt – Ilm ± Po; (3) a layer up to 0.5 cm thick composed of Grt($\mathrm{Alm_{54-58}Prp_{21-26}Sps_{12-21}Grs_4}$) – Qtz – Rt – Ilm ± Ap; (4) a layer up to 1.5 cm thick composed of Grt($\mathrm{Alm_{44-55}Prp_{17-22}Sps_{19-35}Grs_{4-5}}$) – Qtz ± Ilm – Ap ± Po ± Py; and (5) a core up to 7 cm thick composed of Grt($\mathrm{Alm_{40-42}Prp_{12-15}Sps_{38-42}Grs_{5-7}}$) – Qtz – Ilm – Ap – Py – Po ± Ccp ± Kfs ± Mag. Layers 4 and 5 show high Mn, Fe, Mg, P and Ce relative to compositions of average shale. The data appear to be consistent with a hydrogenous–diagenetic origin as opposed to a volcanogenic–exhalative hydrothermal origin. A protolith for the Mn-rich portions of the pod could have been an early diagenetic Mn–Fe-bearing carbonate concretion, with detrital quartz and clay as a source for aluminum. Garnet-producing reactions probably began in the Mn-rich pod interior and progressed outward as garnet became stable in more Mn-poor environments. Individual grains of garnet in the pelitic schist (1) and pod core (5) are essentially homogeneous, presumably owing to high rates of diffusion at peak metamorphism. However, garnet grains in the intervening layers (2 – 4) preserve steep nonconcentric compositional gradients radial to the pod core. It is proposed that diffusion failed to homogenize the garnet in layers 2 – 4 owing to strong compositional gradients already present between the manganiferous core material and the surrounding shales. Intragranular diffusion appears to have been the dominant diffusional process during the late stages of regional metamorphism; it allowed the preservation of a range of garnet compositions over a distance of 6 cm.

Keywords: coticule, spessartine garnet, granulite facies, diffusion, Rangeley Formation, Massachusetts.

SOMMAIRE

Une lentille distinctive à grenat (spessartine) + quartz, appelée "coticule", mesurant 14 × 12 × 11 cm et située dans les schistes pélitiques métamorphisés aux conditions du facies granulite de la Formation de Rangeley (âge silurien), dans la partie sud-centrale du Massachusetts, a fait l'objet d'une étude approfondie pour en déterminer le protolithe et son évolution géochimique et minéralogique. La lentille est stratifiée de façon symétrique à l'échelle macroscopique aussi bien qu'à l'échelle microscopique. Le schiste pélitique encaissant contient Qtz – Pl – Kfs – Grt($\mathrm{Alm_{60-63}Prp_{26-27}Sps_{8-10}Grs_4}$) – Bt – Sil ± Ilm ± Po ± Ap. Un niveau quartzofeldspathique externe de 0.5 à 2.5 cm en épaisseur contient Qtz – Kfs – Pl – Grt($\mathrm{Alm_{58-60}Prp_{27}Sps_{10-11}Grs_4}$) – Rt – Ilm ± Po. Vers le centre, il y a ensuite un niveau d'une épaisseur de 0.5 cm qui contient Grt($\mathrm{Alm_{54-58}Prp_{21-26}Sps_{12-21}Grs_4}$) – Qtz – Rt – Ilm ± Ap, un niveau d'une épaisseur de 1.5 cm qui contient Grt($\mathrm{Alm_{44-55}Prp_{17-22}Sps_{19-35}Grs_{4-5}}$) – Qtz ± Ilm – Ap ± Po ± Py, et un coeur d'une épaisseur de 7 cm qui contient Grt($\mathrm{Alm_{40-42}Prp_{12-15}Sps_{38-42}Grs_{5-7}}$) – Qtz – Ilm – Ap – Py – Po ± Ccp ± Kfs ± Mag. Les deux dernières lithologies ont des teneurs élevées en Mn, Fe, Mg, P et Ce comparées au shale moyen. Les données semble indiquer une origine hydrogénétique – diagénétique plutôt que volcanogénique – exhalative et hydrothermale. Un protolithe approprié aux portions riches en Mn serait une concrétion carbonatée d'âge diagénétique précoce, riche en Mn et Fe, avec quartz détritique; une argile rendrait compte de l'aluminium. Les réactions responsables de la production du grenat ont probablement été amorcées à l'intérieur de la lentille, relativement manganifère, pour ensuite progresser vers l'extérieur à mesure que le grenat devenait de plus en plus stable dans les milieux appauvris en Mn. Les grains individuels de grenat dans le schiste encaissant et dans le coeur sont quasiment homogènes, présumément à cause des taux élevés de diffusion aux conditions du paroxysme métamorphique. Toutefois, les grains de grenat dans les niveaux intermédiaires conservent un gradient de composition abrupt, non concentrique, et radiaire autour du coeur de la lentille. La diffusion aurait été inefficace dans ces niveaux intermédiaires pour effectuer la homogénéisation du grenat, vus les gradients abrupts de composition qui existaient déjà entre le coeur manganifère et les shales encaissants. Une diffusion intergranulaire semble avoir été dominante pendant les derniers stades du métamorphisme régional, ce qui a permis la conservation d'une gamme de compositions de grenat sur une distance de 6 cm.

(Traduit par la Rédaction)

Mots-clés: coticule, grenat, spessartine, facies granulite, diffusion, Formation de Rangeley, Massachusetts.

INTRODUCTION

Coticules, or garnet-rich quartzites, are chemically distinctive lithologies of controversial origin. The term *coticule* is primarily a field term used to describe pink to purple, fine-grained garnet-rich granulites (Docka 1985). They are typically more manganoan than average pelite or shale, and commonly, though not always, contain spessartine-rich garnet. The abundance of spessartine-rich garnet reflects the bulk composition of a coticule's protolith. A variety of protoliths have been proposed: manganese-rich sandy layers (Clifford 1960), impure manganiferous chert (Emerson 1898, Schiller & Taylor 1965, Eusden *et al.* 1984, Thompson 1985), manganese carbonate concretions (Woodland 1939, Bennett 1989), and manganiferous sediment with volcanogenic affiliations (Kramm 1976, Lamens *et al.* 1986). The main problem in determining the protolith of these distinctive rocks is that their mineralogy, major- and trace-element chemistry and textural features have been altered by burial, diagenesis and metamorphism.

Although many compositions of coticules have been reported in the literature, particularly in the last ten years (Clifford 1960, Kay 1975, Cranshaw 1982, Docka 1985, Lamens *et al.* 1986, Bennett 1987, Spry 1990), few detailed electron-microprobe data on individual garnet grains are available. Where data are available, most authors indicate that the garnet in the coticule is essentially homogeneous, but they typically show no microprobe traverses across individual garnet grains, nor do they indicate where individual analyses were collected (Kramm 1976, Docka 1985, Spry 1990).

This paper presents major- and trace-element data from four mineralogically distinct layers in a single symmetrically layered pod-shaped coticule in granulite-facies pelitic schist in south-central Massachusetts. The compositions of the two innermost garnetiferous layers are used to place constraints on a possible protolith. Results of detailed electron-microprobe traverses of individual grains of garnet in each layer are used to understand garnet-producing reactions and diffusional processes that have operated during regional metamorphism. A qualitative diffusional model is presented.

BACKGROUND

Coticules were petrographically described for the first time by Renard (1878). They have since been reported in the New England Appalachians and southwestern Caledonides by many authors (Robinson 1963, Huntington 1975, Hatch *et al.* 1983, Kennan & Kennedy 1983, Docka 1984, 1985, Robinson *et al.* 1988, Wonder *et al.* 1988, Spry 1990). In addition to garnet, coticules may contain other relatively Mn-rich (amphibole, biotite, epidote) or Mn-poor (dioctahedral mica, feldspar, tourmaline, chlorite) silicates as well as oxides, sulfides, and manganese-rich carbonate.

Most coticules described in the literature are found within pelitic schists in low- to medium-grade terranes (Bennett 1989). The sample discussed herein (P114B) is from an Acadian granulite-facies assemblage in Zone VI, the garnet – cordierite – sillimanite – K-feldspar zone of Tracy (1975, 1978). The spessartine content of the garnet (up to 42%) within the core of this garnet–quartz pod is the highest found to date in Zone VI (P. Robinson, pers. comm., 1990), although considerably lower than the 64% reported in a coticule in Zone II (sillimanite–staurolite zone) by Huntington (1975).

Geological and structural setting

Sample P114B was collected from the Tenneco Gas Corporation pipeline trench in south-central Massachusetts, 4.4 km S50°W of Sturbridge (Fig. 1). Mapping by Berry (1989) shows that the sample belongs to the upper part of the Silurian Rangeley Formation (Brimfield Member), which consists primarily of Qtz–Pl–Kfs–Bt–Sil–Grt ± Crd–Gr–Po schists and gneisses (symbols after Kretz 1983).

The sample is located within the Merrimack synclinorium of south-central Massachusetts, which is characterized by Silurian and Devonian sedimentary rocks and pre-Silurian basement units intensely deformed and metamorphosed during the Devonian Acadian orogeny. Based on a detailed stratigraphic and lithological study, Berry (1985, 1987a,b, 1989) suggested that some of the units in the Sturbridge area correlate with Silurian units of New Hampshire and western Maine (Hatch *et al.* 1983). In addition to pelitic schists, gneisses and calc-silicate granulites, Berry identified a sequence of gneiss units interpreted to be pre-Silurian "basement" rocks upon which the stratified rocks were deposited (Berry 1988, Berry & Robinson 1989).

Berry (1989) proposed a revised structural and tectonic model for the Acadian evolution of the Merrimack synclinorium in south-central Massachusetts on the basis of the above stratigraphic interpretations. The area is characterized by three major stages of deformation (Thompson 1985, Thompson *et al.* 1987, Berry 1988, 1989). The earliest structural features observed are west-directed fold-nappes truncated by thrust-nappes of the Acadian nappe stage of deformation. Acadian tonalites, which cross-cut the thrust-nappes, were affected by the peak of granulite-facies metamorphism, which places the peak of metamorphism

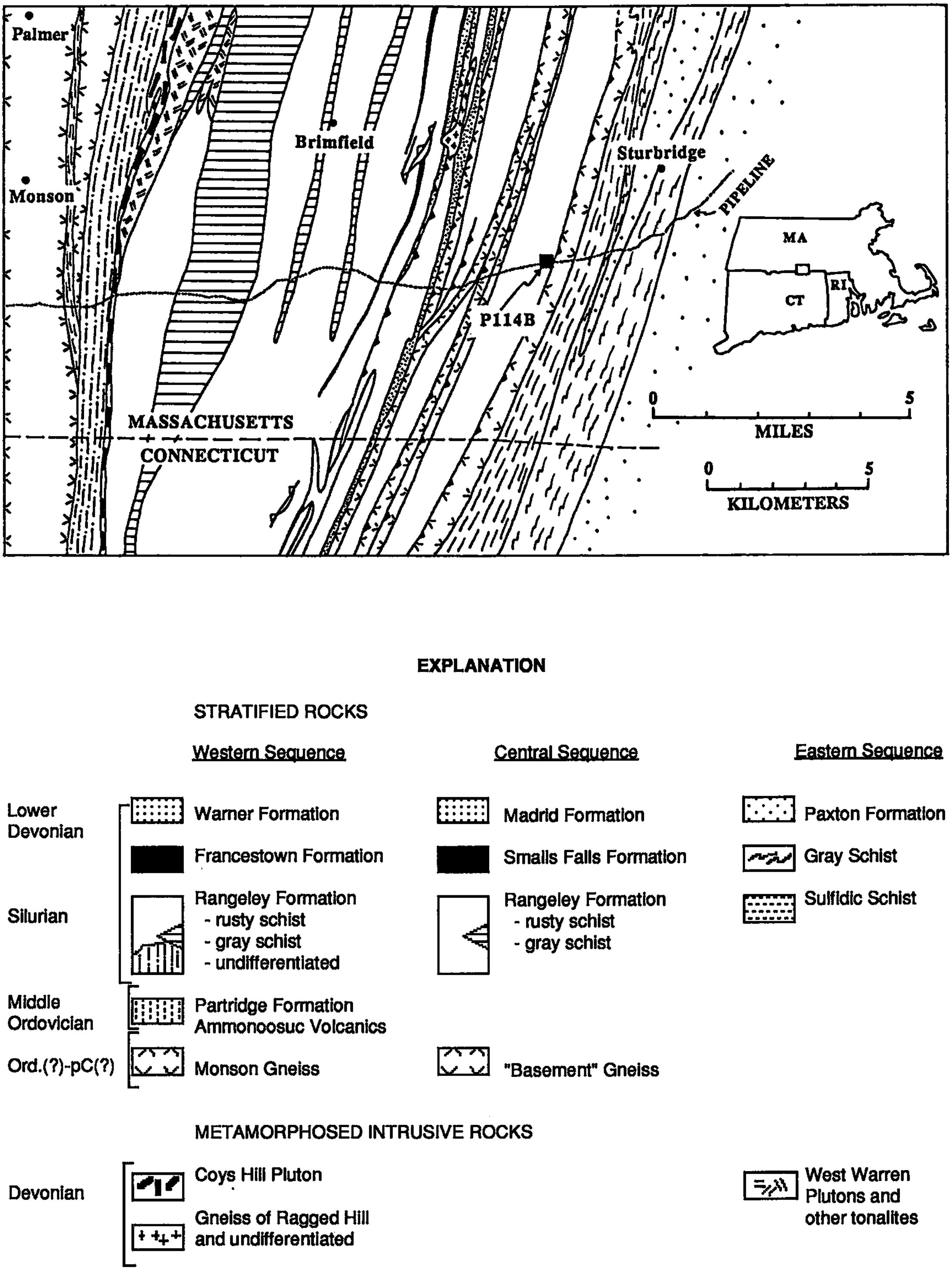

FIG. 1. Generalized geological map of part of the Merrimack synclinorium in south-central Massachusetts, showing location of sample P114B.

after the nappe stage of deformation. The post-granulite facies backfold stage overturned the thrust duplex structure to the east, and mylonites, east–west-trending mineral lineations and isoclinal folds were formed. Finally, asymmetrical, north–south-trending folds were formed contemporaneously with the rise of gneiss domes in the Bronson Hill anticlinorium during the dome stage of deformation or extension of already uplifted basement and cover (Peterson 1992).

Metamorphic evolution

The Merrimack synclinorium is characterized by a counterclockwise P–T path in which compression with heating appears to have been followed by further compression with cooling (Schumacher *et al.* 1989, Thomson 1989, Robinson *et al.* 1989, Berry 1991, Winslow *et al.* 1991). The area is characterized by an early low P – high T metamorphism, which produced andalusite, now rarely preserved in pseudomorphs, in northern Connecticut, central Massachusetts and New Hampshire (Robinson *et al.* 1982). The formation of cordierite-bearing pegmatites by partial melting and dehydration is believed to have been a result of this early metamorphism (Tracy & Dietsch 1982, Schumacher *et al.* 1989, Thomson 1989). Later granulite-facies regional metamorphism affected much of the central part of the Merrimack synclinorium in south-central Massachusetts. Peak conditions for this area have been estimated at 700°C and 6.4 kbar (Robinson *et al.* 1986, Thomson 1989). Fe-rich cordierite within the pegmatites did not re-equilibrate during peak conditions in the granulite facies, as recorded in the surrounding gneisses, but did respond by symplectite formation during cooling at higher pressures (Tracy & Dietsch 1982, Thomson 1989).

DESCRIPTION OF THE GARNET POD

Sample P114B is pod-shaped, 5 to 14 cm in width if viewed parallel to the macroscopic layering and perpendicular to the long axis of the pod (Fig. 2). Only part of the pod was collected; exact

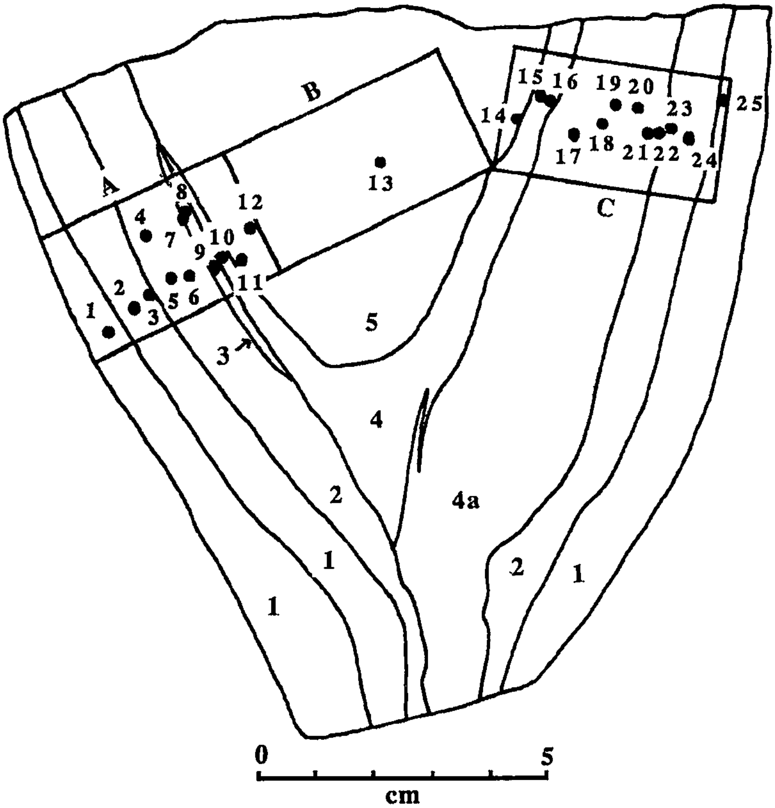

FIG. 2. Macroscopic layering observed on cut surface of the garnet pod. Layers 1 – 5 are discussed in the text. Outlines of three thin sections and locations of analyzed grains 1 – 25 also are shown.

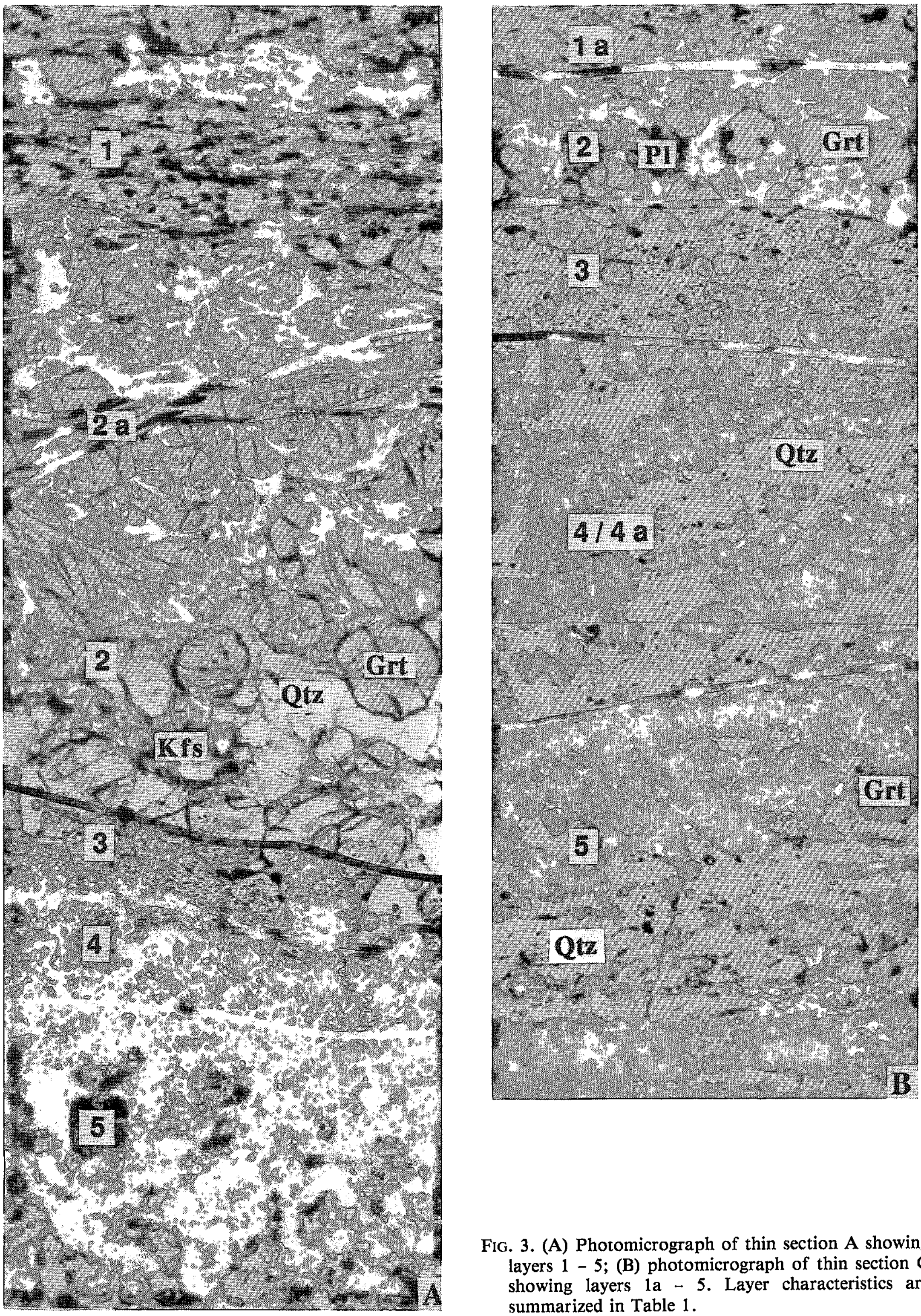

FIG. 3. (A) Photomicrograph of thin section A showing layers 1 - 5; (B) photomicrograph of thin section C showing layers 1a - 5. Layer characteristics are summarized in Table 1.

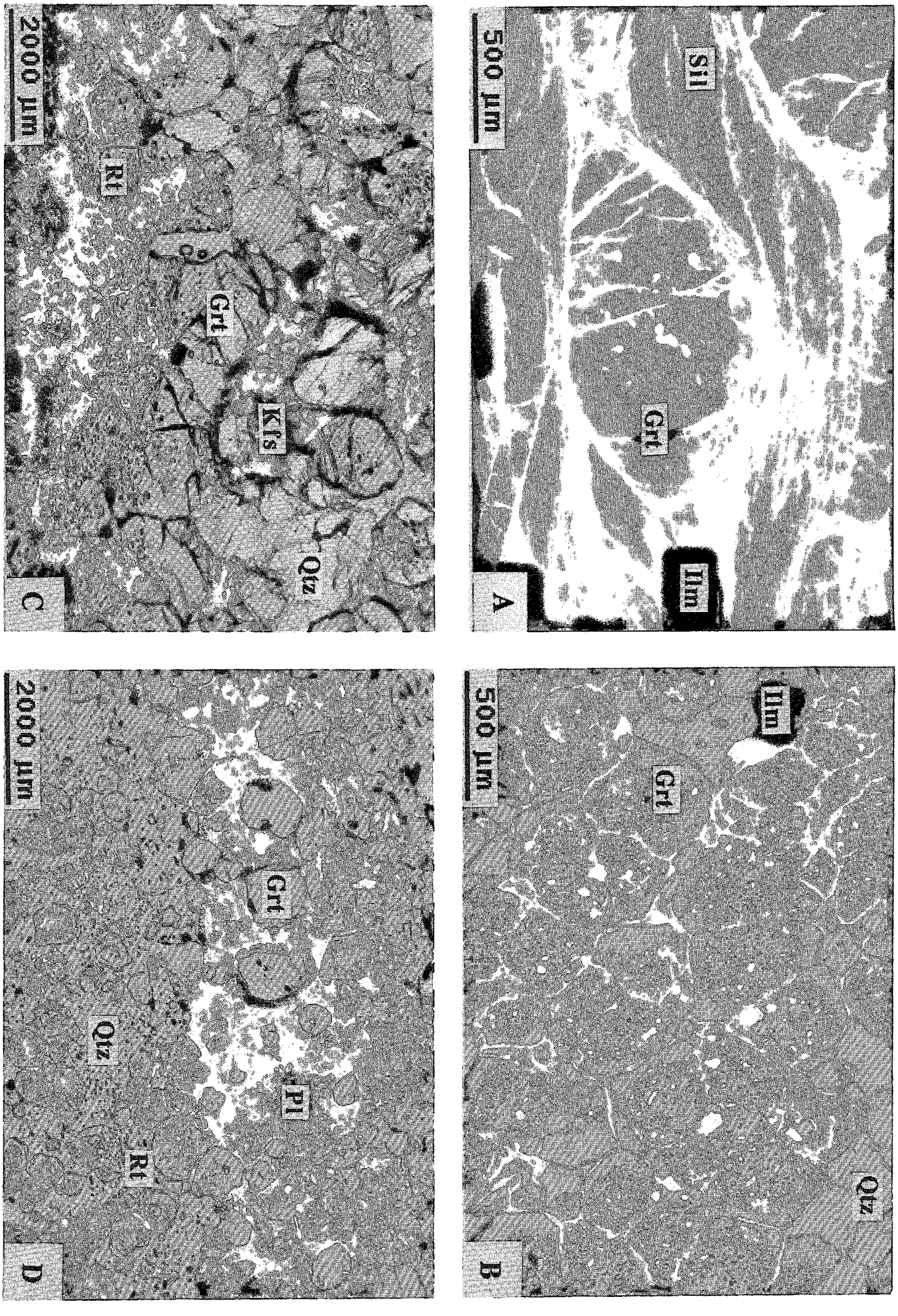
A
Ilm
Grt
Sil
500 µm
B
Ilm
Grt
Qtz
500 µm
C
Qtz
Kfs
Grt
Rt
2000 µm
D
Rt
Pl
Qtz
Grt
2000 µm

FIG. 4. Photomicrographs of layers in thin sections. (A) Layer 2a, TSA; (B) layer 5, TSB; (C) layer 2 (top) and layer 3 (bottom), TSA; (D) layer 2 (top) and layer 3 (bottom), TSC. Layer characteristics are summarized in Table 1.

dimensions could not be determined. Sample P114B was not collected with a record of its field orientation, but the observed layers of the pod are approximately parallel to the strike (N0°E to N30°E) and dip (40° to 70°W) of the surrounding schists and gneisses (Berry 1989).

The pod is symmetrically layered on both a macroscopic and microscopic scale (Fig. 2). The layers range in width from 1 to 25 mm, with a core layer approximately 7 cm thick. The macroscopic layers, distinguished primarily on the basis of size and color of the garnet, are briefly described below.

Layer 1 is a Qtz - Pl - Kfs - Grt - Bt - Sil ± Ilm ± Po ± Ap gneisses layer typical of the surrounding schists and gneisses in the area. Layer 2 is quartzofeldspathic with pink to lavender grains of garnet up to 2 mm across, which are coarser and less abundant than those observed in the interior of the pod. The boundary between layer 2 and layers 4 or 4a is sharp, and particularly well defined between layers 2 and 4 by a very thin (< 1 mm) black layer designated as layer 3, which is rich in rutile. Layer 4 consists primarily of garnet with a distinctive lavender color that is more pronounced where adjacent to layer 3. Layer 4a, observed on one side of the garnet pod, represents a layer of lavender garnet grains like those in layer 4. However, layer 4a appears to have been somewhat deformed or sheared, and garnet grains occur as streaky patches at various angles to the layering. Layer 5, the core of the pod, contains 80–90% garnet, has a fine-grained sugary texture, and is black.

Detailed petrography of layers observed in thin sections A, B and C (Figs. 2, 3, 4) suggest several distinctive similarities. Table 1 summarizes the similarities in terms of mineralogy, garnet characteristics and other textural features of the layers observed in thin sections A, B and C. Table 1 suggests that the garnet pod is approximately symmetrical with respect to microscopic layering.

TABLE 1. SUMMARY OF MICROSCOPIC LAYERING OBSERVED IN THIN SECTIONS A, B and C

Layer		Mineralogy	Garnet Characteristics	Other Textures
1	A	Qtz-Pl-Kfs-Grt-Bt-Sil-Ilm-Po-Ap	0.5 - 5.0 mm. Rare inclusions.	Po > Ilm near layer 2a.
1	C	Qtz-Pl-Kfs-Grt-Bt-Sil-Ilm-Po-Ap	< 2 mm. Rare inclusions.	
1a	C	Qtz-Pl-Kfs-Grt-Bt-Ilm-Po-Ap-Rt	0.25 - 1 mm. Qtz and rare Rt inclusions in Grt cores.	Sil-out. Rare Rt in matrix, increases toward layer 2. Pl sericitized.
2a	A	Sil-Grt-Ilm-Rt	2 mm length x 0.25 - 0.75 width. Rare inclusions of Ilm and Rt.	Bt-out, Rt-in. Fine-grained matrix of felty prismatic Sil and Rt-Ilm aggregates. (Fig. 4a)
2	A	Qtz-Kfs-Pl-Grt-Rt-Ilm-Po	< 2 mm. Rt exsolution lamellae on {111}. Rare Rt and Ilm inclusions in Grt cores.	Sil-out. Coarse-grained matrix of interlocking Qtz-Kfs-Pl. Pl and Kfs are sericitized. Rare sulfides. (Fig. 4c)
2	C	Qtz-Kfs-Pl-Grt-Rt-Ilm-Po	0.5 - 1.0 mm. Rt exsolution lamellae on {111}. Rare Rt inclusions.	Bt-out. Rt weakly aligned parallel to pod layering and is included in Qtz and Pl. Rare Ilm. (Fig. 4d)
3	A	Grt-Rt-Ilm-Qtz	< 1.5 mm. Abundant Rt inclusions aligned parallel to layering. Rt exsolution lamellae on {111}.	Little to no matrix material. (Fig. 4c)
3	C	Qtz-Grt-Rt-Ilm-Ap	0.25 - 1.0 mm. Rare inclusions.	Matrix primarily Qtz. Rt aligned parallel to layering. Rare Ilm. (Fig. 4d)
4	A	Grt-Qtz-Ilm-Ap-Po-Py	< 0.25 mm. Grt to 90%. Inclusions of Qtz and Ap. Rare Ilm and sulfide inclusions.	Coarse Ilm abundant adjacent to layer 3. Rare Rt. Matrix primarily Qtz (5-10%).
4 / 4a	C	Qtz-Grt-Ilm-Ap-Po-Py	0.25 - 0.5 mm. Inclusions of Qtz and Ap in cores or throughout.	Abundant Ap. Rt absent. Matrix primarily Qtz.
5	A,B, & C	Grt-Qtz-Ilm-Ap-Py-Po-Ccp-Kfs-Mag	0.25 - 1.0 mm. Grt 75 - 90%. Inclusions of Py-Po, Ilm and lesser amounts of Qtz and Ap. Inclusion-rich cores, inclusion-free rims. Coalesced grains often share a common inclusion-free rim.	Matrix primarily Qtz. Mag and Ccp rare. Rare sericitized Kfs in matrix. (Fig. 4b)

Layer 1 = pelitic schist; Layer 2 = quartzofeldspathic layer; Layer 3 = rutile-rich layer; Layer 4, 4/4a = lavender-colored garnet layer; 5 = pod core. A, B and C = thin sections. Mineral abbreviations from Kretz (1983).

METHODS OF STUDY

Three polished thin sections were prepared from a single slab cut perpendicular to the layering of the pod (Fig. 2). Electron-microprobe analyses of garnet (locations shown in Fig. 2), biotite, plagioclase, ilmenite and rutile were performed on the JEOL-733 five-spectrometer Superprobe housed at Rensselaer Polytechnic Institute in Troy, New York, using both natural and synthetic mineral standards. The operating conditions for analyses were: accelerating potential 15 kV, beam current 15 nA. A beam diameter of 1 to 5 μm was used for garnet, rutile and ilmenite, and 10 μm for biotite and plagioclase. Raw data were corrected using the method of Bence & Albee (1968), with the alpha factors of Albee & Ray (1970). Garnet compositions are presented in this paper. Tables of analytical data on biotite, plagioclase and ilmenite are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

A second slab of the garnet pod was carefully separated into four samples by trim saw. Small chips were collected from the pelitic schist layer (Sample 1), the quartzofeldspathic + rutile layers (Sample 2/3), the layers containing lavender-colored garnet (Sample 4/4a), and the pod core (Sample 5) (Fig. 2). Each chip was ground on silicon carbide 240 grit to remove saw marks or material from adjacent layers. Samples selected for major- and trace-element analysis were prepared

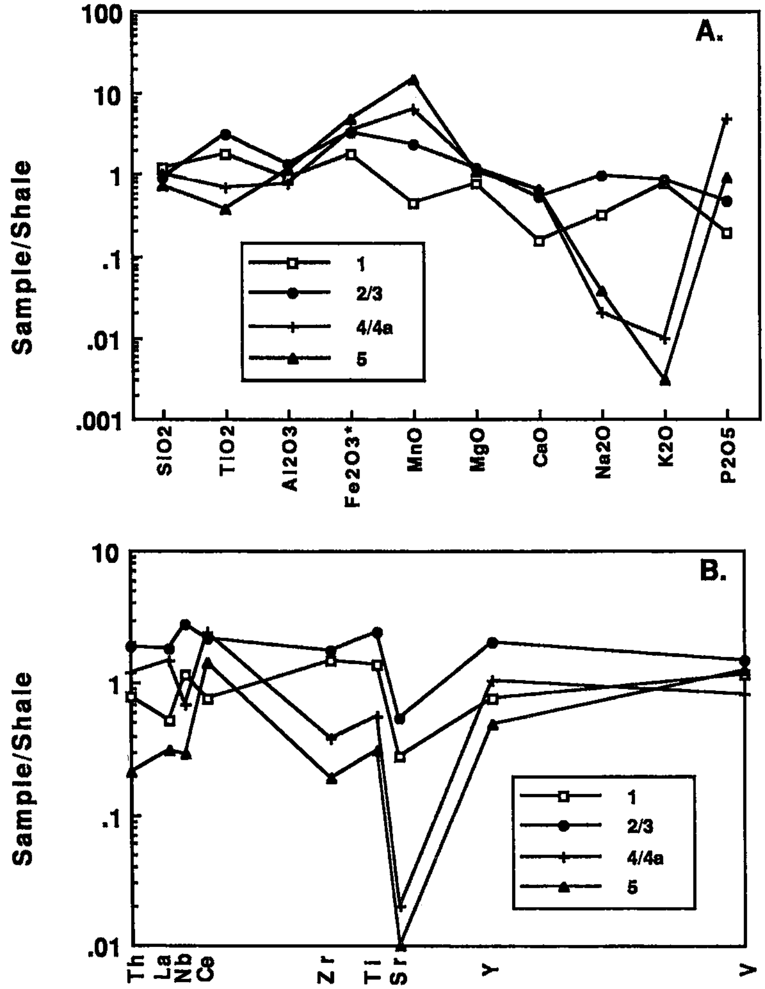

FIG. 5. Major- (A) and trace-element (B) diagrams of data from samples 1, 2/3, 4/4a and 5 normalized to composition of average shale, taken from Blatt *et al.* (1980, Table 11-2). Order and positions of trace elements from Bougault (1980).

TABLE 2. MAJOR- AND TRACE-ELEMENT DATA FOR SAMPLES 1, 2/3, 4/4a AND 5 COMPARED TO NEW ENGLAND COTICULES AND AVERAGE SHALE COMPOSITION

	1	2/3	4/4a	5	Coticules	Avg. Shale
SiO_2	71.59	52.55	60.87	43.48	53.2-70.3	58.1
TiO_2	1.05	1.84	0.43	0.23	0.1-0.6	0.6
Al_2O_3	13.92	21.07	11.96	17.72	7.8-16.5	15.4
Fe_2O_3*	7.11	13.59	14.39	19.25	10.6-20.1	4.0
FeO	-	-	-	-	-	2.4
MnO	0.45	2.43	6.30	14.64	3.9-8.4	tr
MgO	1.82	2.97	2.90	2.66	1.0-1.9	2.4
CaO	0.47	1.63	2.08	1.98	1.4-4.2	3.1
Na_2O	0.40	1.25	0.03	0.05	0.0-2.1	1.3
K_2O	2.54	2.81	0.04	0.01	0.1-1.1	3.2
P_2O_5	0.04	0.09	0.97	0.18	-	0.2
Total	99.39	100.22	99.97	100.20	-	-
V	149.9	194.6	104.7	163.5	88-212	130
Cr	89.8	145.7	50.9	10.8	44-112	100
Ni	73.9	30.7	19.6	62.2	8-88	80
Zn	113.0	83.1	104.4	115.3	44-184	90
Ga	19.3	24.9	8.6	19.7	-	25
Rb	106.4	87.6	1.8	0.4	-	140
Sr [Au]	112.7	215.1	7.6	2.2	-	400
Sr [Mo]	119.2	231.8	6.8	2.2	-	400
Y	27.3	71.4	36.3	17.0	-	35
Zr	267.5	315.3	67.6	33.5	-	180
Nb	17.5	41.0	10.2	4.3	-	15
Ba	553.7	738.1	12.2	19.5	144-686	600
La	20.9	72.1	59.8	12.6	17-26 D	40
Ce	53.1	150.6	169.3	99.4	57-72 D	70
Pb	13.8	28.2	4.2	3.0	-	20
Th	9.4	22.9	14.3	2.6	-	12
U	2.3	5.1	4.2	0.0	-	3.5
Ce/Y	1.9	2.1	4.7	5.9	-	-
Ce/La	2.5	2.1	2.8	7.9	-	-
U/Th	0.2	0.2	0.3	0.0	-	-
Mn/Fe	0.1	0.2	0.4	0.8	-	-

Oxides in wt. %, trace elements in ppm. Coticules: Data from Cranshaw (1982)
Fe_2O_3* = FeO + Fe_2O_3 D = Docka (1985)
1 = pelitic schist
2/3 = quartzofeldspathic + rutile
4/4a = lavender-colored garnet layer
5 = pod core
Average Shale: Major-element data from Blatt et al. (1980)
Average Shale: Trace-element data from Krauskopf (1979)

using modifications of the methods of Norrish & Chappell (1967) and Norrish & Hutton (1969). Major-element analyses were performed on an automated Siemens X-ray fluorescence spectrograph using a Rh tube. Trace-element analyses were performed on an automated Siemens sequential X-ray fluorescence spectrograph using a Au tube (Nb, Zr, Zn, Ni, Cr, V, Ce, Ba, La, Sr) or Mo tube (Y, Sr, U, Rb, Th, Pb, Ga). Both instruments are housed at the University of Massachusetts. Major- and trace-element analyses were performed on sample numbers 1, 2/3, 4/4a and 5 (Table 2, Fig. 5).

MAJOR- AND TRACE-ELEMENT CHEMISTRY

Major elements

As one would expect, the mineralogy in each layer is a reflection of its bulk composition. For example, the presence of abundant K-feldspar, plagioclase and rutile in sample 2/3 reflects high K, Na, Al and Ti. Similarly, the high modal percent of apatite in the layer of the pod containing lavender-colored garnet (Sample 4/4a) reflects high P and Ca.

Manganese increases from 0.45 to 14.64 wt.% from the pelitic schist (Sample 1) to the core of the pod (Sample 5). The high Mn content accounts for the presence of substantial spessartine garnet in the pod's core. In fact, of the whole-rock geochemical data available for New England coticules (Clifford 1960, Cranshaw 1982) shown in Table 2 for comparison, the core of the pod has the highest concentration of Mn. Magnesium and Fe content variation from layer to layer is reflected in modal variations of minerals, particularly of garnet.

Trace elements

The trace-element pattern defined by samples 4/4a and 5 are similar, as are the patterns defined by samples 1 and 2/3 (Fig. 5b). With the exception of Th, La, Nb and Ce, all four samples are analogous in terms of observed positive and negative anomalies relative to average shale compositions (Krauskopf 1979). Samples 4/4a and 5 differ from samples 1 and 2/3 in that they are characterized by a slight positive cerium anomaly and a slight negative niobium anomaly. The positive cerium anomaly, which is larger in sample 4/4a, reflects abundant apatite in the lavender-colored garnet layers. A small positive cerium anomaly also was determined for coticules studied by Docka (1985) if normalized to chondrite values. However, Docka (1985) stated that samples studied show that Ce is depleted relative to shales. This is not the case for samples 4/4a and 5, which show a strong positive Ce anomaly if chondrite-normalized (enrichment 100 times chondrite) as well as a slight positive Ce anomaly if normalized to shale. Niobium is considerably depleted in sample 5, and to a lesser extent in sample 4/4a, but shows a slight positive anomaly in sample 2/3. This feature may be explained by the abundance of rutile in sample 2/3, the quartzofeldspathic and rutile-bearing layers.

Concentrations of trace elements not depicted in Figure 5b (Cr, Ni, Zn, Ga, Rb, Ba, Pb and U), are generally low with respect to average shale compositions, with the following exceptions. Barium and chromium concentrations in sample 2/3 are high relative to shales and all other samples from the pod. Although K-feldspar was not analyzed by electron microprobe, the high Ba concentration in sample 2/3 is assumed to be reflected by its abundance. The high Cr concentration may be explained in terms of possible substitution into garnet or rutile, although this has not been substantiated by analysis. Zn is high in both 4/4a and 5, and is presumably present in chalcopyrite (see Table 1).

In summary, and concentrating on samples 4/4a and 5, the major- and trace-element analyses suggest that the bulk chemistry of the coticule pod, in relation to average shale compositions, is characterized by: (1) anomalously high Mn, Fe, P and Mg, (2) a slight positive Ce anomaly, (3) similar V, Si and Al, (4) a slight negative Nb anomaly, (5)

TABLE 3. TYPICAL CORE OR NEAR-CORE COMPOSITIONS OF GARNET GRAINS 1-25 (FIG. 2)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
SiO2	37.33	38.47	38.79	38.04	38.69	38.18	38.04	38.64	38.09	37.40	37.26	38.02	38.24	37.15	36.46	36.90	36.71	37.90	37.90	37.66	38.18	38.47	38.14	38.44	36.80
Al2O3	21.91	22.18	22.35	21.74	22.29	21.73	21.72	21.80	21.93	21.63	21.71	21.60	22.74	21.38	21.25	21.29	21.07	21.75	21.68	21.76	21.96	22.00	22.33	22.15	21.89
MgO	6.68	6.71	6.96	6.96	7.21	6.76	5.96	5.66	5.43	4.79	4.25	3.79	3.02	3.06	2.99	3.09	3.82	4.46	4.42	5.81	5.92	6.95	7.08	7.11	6.78
FeO	28.67	28.88	27.91	26.99	27.48	26.39	27.03	26.09	24.92	23.92	22.62	19.26	18.36	18.80	18.43	18.30	19.71	20.00	21.60	25.83	25.92	27.39	27.41	28.18	28.78
MnO	3.37	3.98	4.28	4.45	4.77	5.02	6.64	7.91	9.43	10.92	13.59	17.62	17.39	19.15	18.82	18.74	17.65	16.42	14.72	8.46	8.13	5.52	5.12	4.6	3.62
CaO	1.41	1.44	1.45	1.44	1.46	1.47	1.42	1.49	1.51	1.54	1.57	1.63	2.14	2.35	2.45	2.42	1.89	1.63	1.51	1.58	1.48	1.50	1.48	1.41	1.33
Total	99.37	101.67	101.75	99.62	101.90	99.56	100.82	101.59	101.31	100.21	101.01	101.93	101.88	101.88	100.40	100.75	100.86	102.17	101.84	101.11	101.59	101.82	101.55	101.90	99.20
Si	2.953	2.974	2.984	2.988	2.974	2.999	2.981	3.004	2.978	2.970	2.954	2.988	2.988	2.950	2.938	2.955	2.940	2.967	2.975	2.955	2.972	2.971	2.950	2.964	2.926
Al	2.042	2.021	2.027	2.012	2.019	2.012	2.006	1.997	2.021	2.025	2.029	2.001	2.094	2.001	2.018	2.010	1.989	2.007	2.006	2.012	2.015	2.003	2.035	2.013	2.050
Mg	0.788	0.774	0.798	0.815	0.827	0.792	0.697	0.656	0.633	0.568	0.502	0.445	0.351	0.362	0.359	0.369	0.456	0.521	0.517	0.680	0.687	0.800	0.816	0.818	0.803
Fe	1.897	1.867	1.795	1.773	1.766	1.734	1.771	1.696	1.629	1.589	1.500	1.266	1.200	1.248	1.242	1.226	1.320	1.309	1.418	1.695	1.687	1.769	1.773	1.817	1.913
Mn	0.226	0.261	0.279	0.296	0.310	0.334	0.441	0.521	0.624	0.735	0.913	1.173	1.151	1.288	1.284	1.272	1.197	1.089	0.979	0.562	0.536	0.361	0.335	0.301	0.244
Ca	0.119	0.119	0.119	0.121	0.120	0.123	0.119	0.124	0.127	0.131	0.134	0.137	0.179	0.200	0.211	0.208	0.162	0.137	0.127	0.133	0.123	0.124	0.122	0.117	0.113
XFe	0.707	0.707	0.692	0.685	0.681	0.686	0.718	0.721	0.720	0.737	0.749	0.740	0.774	0.775	0.776	0.769	0.743	0.715	0.733	0.714	0.711	0.689	0.685	0.690	0.704
Alm	0.626	0.618	0.600	0.590	0.584	0.581	0.585	0.566	0.541	0.526	0.492	0.419	0.417	0.403	0.401	0.399	0.421	0.428	0.466	0.552	0.556	0.579	0.582	0.595	0.623
Prp	0.260	0.256	0.267	0.271	0.274	0.266	0.230	0.219	0.210	0.188	0.165	0.147	0.122	0.117	0.116	0.120	0.145	0.170	0.170	0.221	0.227	0.262	0.268	0.268	0.261
Sps	0.075	0.086	0.093	0.099	0.103	0.112	0.146	0.174	0.207	0.243	0.299	0.388	0.400	0.416	0.415	0.414	0.382	0.356	0.322	0.183	0.177	0.118	0.110	0.099	0.079
Grs	0.039	0.039	0.040	0.040	0.040	0.041	0.039	0.041	0.042	0.043	0.044	0.045	0.062	0.065	0.068	0.068	0.052	0.045	0.042	0.043	0.041	0.041	0.040	0.038	0.037

Compositions reported as wt.% oxides. Alm almandine, Prp pyrope, Sps spessartine, Grs grossular (reported as mol fractions).

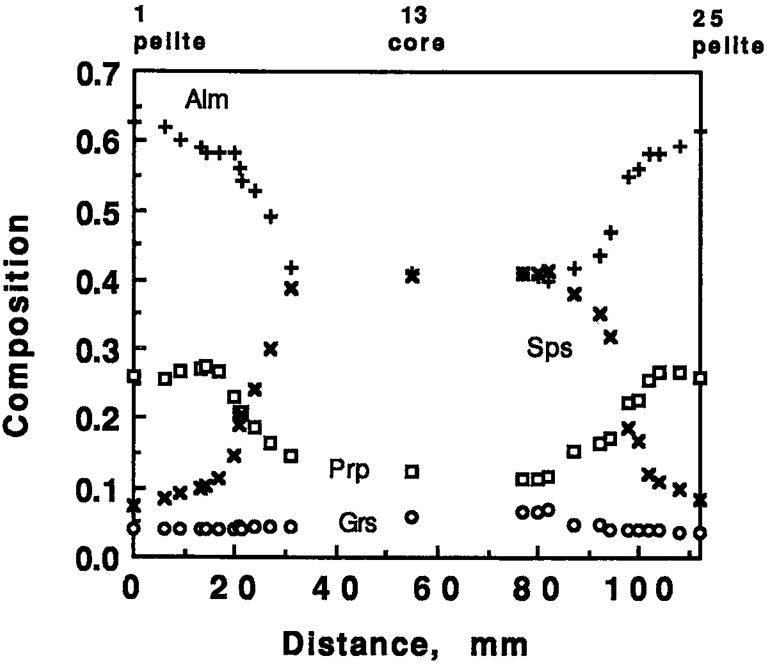

FIG. 6. Garnet compositional variation *versus* distance (mm). Garnet grains 1 – 25 are from left to right with the pod center represented by garnet no. 13. See Figure 2.

low concentrations of Ca, Ti, Cr, Ga, Zr, Pb and Ni, (6) extremely low concentrations of Na, K, Sr, Rb and Ba, (7) slight enrichment (sample 4/4a) or depletion (Sample 5) in La, Y, U and Th, and (8) enrichment in Zn.

MINERAL CHEMISTRY

Garnet

Twenty-five garnet grains ranging in diameter from 0.5 to 1.8 mm were selected for detailed electron-microprobe analysis (Fig. 2). Traverses of one or more grains of garnet from each layer were conducted perpendicular to the layering in the pod. Traverses consisted of 15 to 20 evenly spaced points across the center of each grain, depending on its diameter. Table 3 shows core or near-core compositions of the 25 selected garnet grains in the various layers of the pod. Garnet stoichiometry suggests that iron present in the garnet is predominantly Fe^{2+} and that the amount of Fe^{3+} is negligible or nil.

Distinct compositional differences exist from grain to grain depending on a garnet's location within the pod. The almandine, pyrope and spessartine content are symmetrical with respect to distance, whereas grossular is slightly asymmetrical (Fig. 6). The compositional variation observed within the pod as a whole bears a striking resemblance to the compositional variation observed in single grains of growth-zoned garnet within amphibolite-facies assemblages (Tracy 1975, 1978, Tracy *et al.* 1976) (Fig. 7).

Depending on its location within the pod, garnet is either compositionally homogeneous or nonconcentrically zoned. Figure 8 shows traverses of ten individual grains analyzed in the various layers of the pod in terms of spessartine content *versus* distance (mm) relative to the exterior rim of garnet number 1. Traverses were taken perpendicular to the layering in the pod. Grains are essentially homogeneous in the pelitic schist (1) and in the pod core (5). Spessartine contents vary by only 0 to 0.6% across individual grains from these layers. However, compositional gradients are present in garnet grains of the quartzofeldspathic layer (2), the rutile-rich layer (3) and the lavender-colored garnet layers (4/4a). Spessartine contents vary from 1.0 to 5.0% across individual grains from these layers.

To characterize more fully the observed nonconcentric zoning, compositional maps of selected

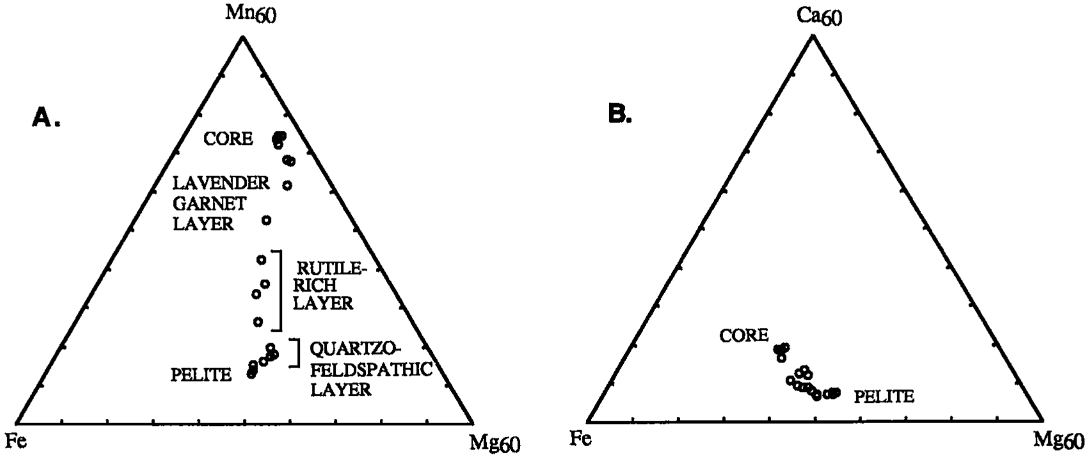

FIG. 7. Fe-Mg$_{60}$-Mn$_{60}$ (A) and Fe-Mg$_{60}$-Ca$_{60}$ (B) triangular plots of 25 garnet grains (cores) analyzed in three thin sections studied.

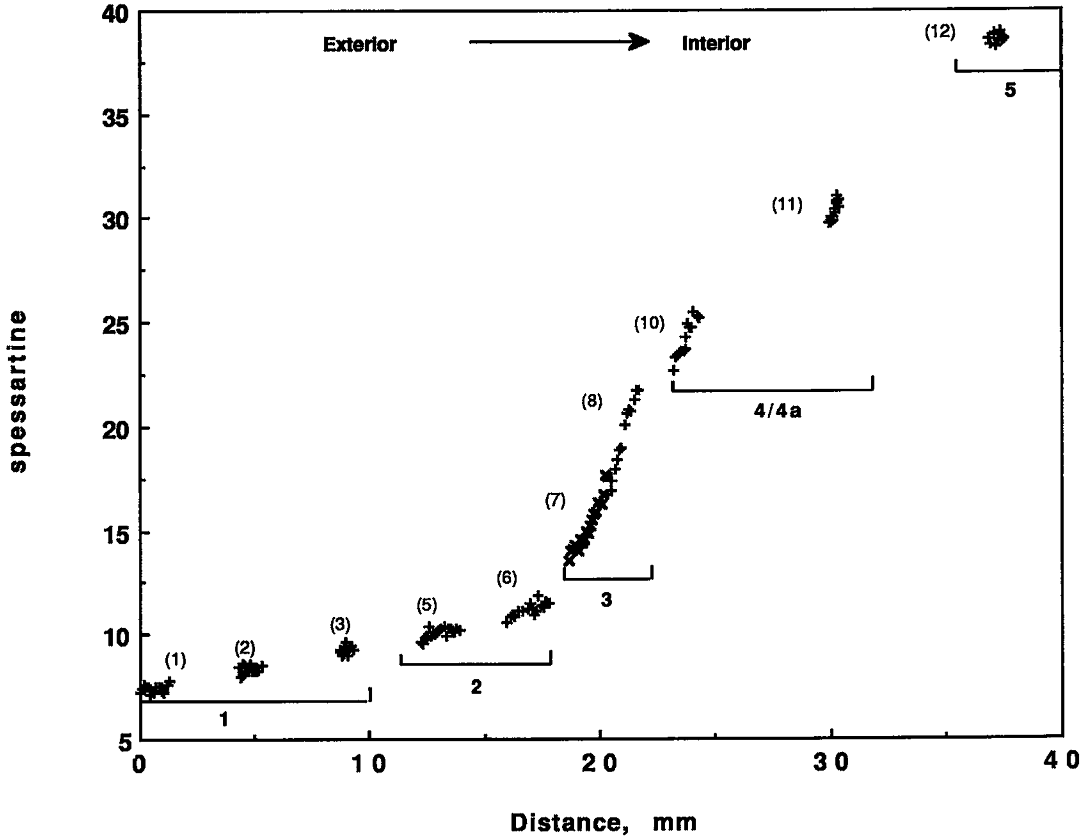

FIG. 8. Traverses of individual grains of garnet in terms of spessartine content *versus* distance (mm). 1 Pelitic schist layer, 2 quartzofeldspathic layer, 3 rutile-rich layer, 4/4a layer of lavender-colored garnet, 5 pod core. Numbers of individual grains of garnet are shown in parentheses (see also Fig. 2).

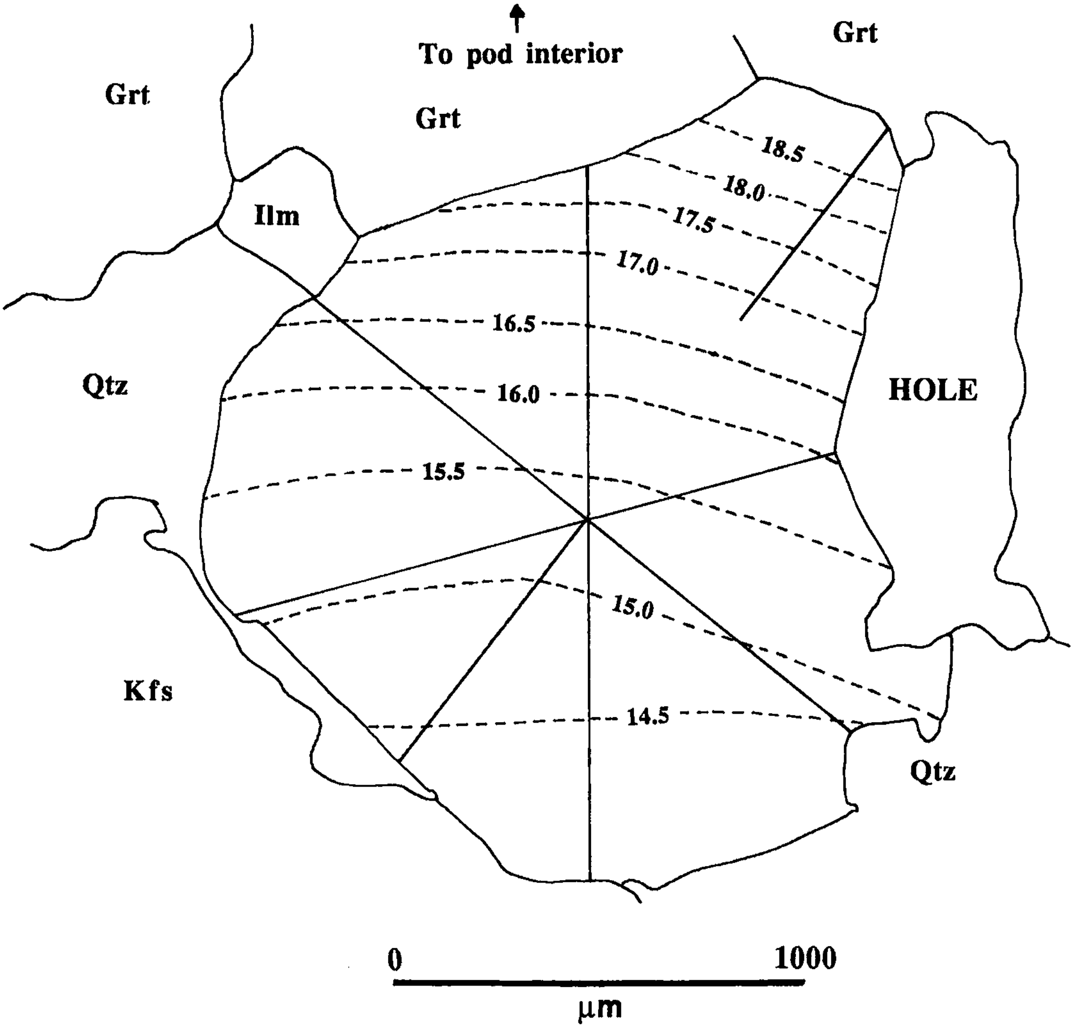

FIG. 9. Nonconcentric contours of spessartine content (dashed lines) for grain no. 7 from the rutile-rich layer of thin section A. Electron-microprobe traverses are shown as solid lines. Analysis spacings are 2 μm near the rim and 25 μm near the core. Qtz quartz, Ilm ilmenite, Grt garnet, Kfs K-feldspar.

grains of garnet were constructed on the basis of several detailed rim-to-core electron-microprobe traverses. A compositional map of spessartine component of grain number 7 (Figs. 2, 8) from layer 3 of thin section A is shown in Figure 9. Spessartine content is highest (18.5%) on the side of the garnet closest to the interior of the pod. Contours are fairly straight and nearly parallel to the layering in the pod. The decrease in spessartine content across the garnet toward the exterior of the pod is accompanied by an increase in both almandine and pyrope components. Grossular content is fairly constant from one side of the garnet to the other. Implications of this zoning will be discussed in a later section.

Biotite

Red-brown to yellow biotite is present in layers 1 and 1a (Fig. 3). Analyses of isolated matrix biotite within each layer show little chemical variation toward the pod interior. The average of ten biotite compositions from the pelitic schist in thin section A give results comparable to matrix biotite compositions of surrounding schists and gneisses, with Fe/(Fe + Mg) = 0.42 and Ti/11 oxygen atoms

Garnet-producing reactions

The variations in mineral composition and mineral assemblages across the garnet pod appear to be primarily a function of differences in bulk composition. It is probably safe to assume that reactant phases at the time of garnet growth were different in different parts of the pod and that garnet-producing reactions did not, by any means, occur simultaneously.

The small grain-size of and abundant inclusions within garnet grains observed within the core of the pod suggest that there were many centers of nucleation and that growth was rapid (Carlson 1989). The initial bulk composition of the pod was most certainly manganiferous, so that garnet forming from such a reservoir also would be manganiferous. The internal patterns of inclusions and the high Mn content of the garnet in the core of the pod strongly imply that these grains began growth at much lower metamorphic grade, and that perhaps they were once strongly zoned. If garnet-producing reactions began in the most Mn-rich portions of the pod, they probably progressed outward, enveloping more of the surrounding rock as garnet became a stable phase in more Mn-poor environments. As more of the available manganese was used up by garnet growth in the center of the pod, less was available for garnet that would form later. The garnet in layers 4/4a (the distinctive lavender-colored garnet layers) is considered to have grown slightly later and less rapidly than the garnet in the core. It probably grew from a reservoir with less manganese and higher Fe/Mg ratio. If the garnet grew more slowly, there would be fewer centers of nucleation, and fewer inclusions would be incorporated in individual grains.

Ilmenite is the primary oxide phase present in both layers 5 and 4/4a, and its occurrence is primarily a reflection of the high iron content of these layers. Rutile, on the other hand, is the primary oxide phase present in the most magnesian bulk composition, specifically layers 2 and 3 of the pod (Sample 2/3, Table 2), although there was enough iron available for the formation of ilmenite as well. The quartzofeldspathic and rutile-bearing layers may have formed by slightly different garnet-producing reactions than those operating at the interior of the pod. One possible garnet-producing reaction that may account for the abundance of K-feldspar as well as the high contents of pyrope in the garnet within the quartzofeldspathic layer is the dehydration reaction of biotite + sillimanite + quartz to give garnet + K-feldspar + H_2O.

Qualitative models of diffusion

Diffusional mass-transfer of material in metamorphic rocks occurs in two different ways: intergranular (grain-boundary) diffusion and intragranular (volume) diffusion. Diffusional processes in garnet are generally not very effective at staurolite grade (550°C) or lower (Loomis 1982). However, intragranular diffusion should become quite effective at temperatures of the upper amphibolite to granulite facies over long periods of time. Intragranular diffusion in garnet becomes important at temperatures above the sillimanite zone (Tracy 1982) and may be important at grades as low as the staurolite or staurolite–kyanite zone (Anderson & Olimpio 1977).

There are many examples of prograde growth-zoned garnet in amphibolite-facies and lower-grade rocks (Tracy 1982, Robinson *et al.* 1982, 1986), where zoning developed owing to continuous or discontinuous changes in composition of garnet-producing reactants or to selective segregation of elements during garnet growth (Hollister 1966). Such zoned garnet is preserved because temperatures were not high enough to allow volume diffusion in the garnet to homogenize the recorded compositions. By analogy with these observations, some grains of garnet within the pod at the early stages of metamorphism and growth may have been compositionally zoned, with a Mn-rich core and a Mn-poor rim, particularly in the pelitic schist layer. Garnet within the core of the pod may have been weakly zoned or unzoned owing to partitioning of Mn into other Mn-minerals that may have been present (*e.g.*, rhodochrosite). It should be noted that compositional profiles could, in fact, be much more complicated than a simple, idealized bell-shape during early growth. During later higher-grade metamorphism, diffusional processes would presumably affect not only individual grains of garnet and other phases in the pod by volume diffusion, but perhaps the entire pod by both grain-boundary and volume diffusion.

As suggested above, the protolith of the pod was probably a manganese–iron-bearing carbonate concretion with detrital quartz and clay surrounded by a more typical shale. A compositional gradient resulting from sedimentary and diagenetic processes as well as early intergranular diffusion probably existed between these two extremes. Garnet that grew in the pod core is the most manganiferous, whereas that in the pelitic schist is the least manganiferous. Garnet in the intervening layers has a spessartine content intermediate between the two and perhaps records the initial compositional gradient imposed by the disparities in bulk composition.

A purpose of this inquiry is to understand the diffusional processes that enabled individual grains of garnet in layers 2, 3 and 4/4a of the pod to obtain and preserve the observed patterns of nonconcentric zoning (Fig. 9). This problem may be easier to address initially if, as a simplification, the entire pod is considered as a single garnet with a radius of 6 cm that was unable to completely homogenize during granulite-facies metamorphism. The matrix phases in the garnet pod might then be thought of as inclusions within this large single growth-zoned garnet. This is not to suggest that the garnet pod actually "behaved" as a large single growth-zoned garnet. This simplification is an end-member model that I have used to try to understand diffusional processes in this rather unusual sample; other models may be applicable. However, I do believe that the methods to calculate the time necessary for the diffusional homogenization of the garnet pod as a whole are similar to the methods used to calculate the time necessary to homogenize a single large grain of garnet. If a garnet grain of this size (6 cm radius) were subjected to granulite-facies metamorphism for a very long time, intragranular diffusion would be unable to completely erase the compositional profile, because the distances over which constituents would have to diffuse are unreasonably large. The problem may be evaluated further by an approximate solution of diffusion equations.

The time necessary for nearly complete homogenization of a zoned garnet crystal is approximated by the relation:

$$x^2 = 4Dt \tag{1}$$

where x is the crystal's radius (m), D the diffusion coefficient (m^2s^{-1}) and t time (s) (Freer 1981). The diffusion coefficient (D) is calculated using the Arrhenius equation:

$$D = D_0 \exp(-E_a/RT) \tag{2}$$

where D_0 is the pre-exponential factor (m^2s^{-1}), E_a the activation energy ($Jmol^{-1}K^{-1}$), R the gas constant ($Jmol^{-1}K^{-1}$), and T, the temperature (K). Solution of this equation allows the calculation of D at any temperature from values of D_0 and E_a in the literature (Lasaga *et al.* 1977, Freer 1981, Ganguly *et al.* 1984, Elphick *et al.* 1985, Cygan & Lasaga 1985, Loomis *et al.* 1985, Chakraborty & Ganguly 1991). Using the data of Lasaga *et al.* (1977) and T = 700°C (973 K), D = 5.12 ™ 10^{-20} m^2s^{-1}. The diffusion data of Lasaga *et al.* (1977) were chosen because they are based on Fe–Mg interdiffusion in natural almandine–pyrope garnet obtained from high-grade metamorphic conditions similar to those in central Massachusetts. These data have been used previously for calculations of diffusion (Tracy & Dietsch 1982) and cooling rate (Lasaga *et al.* 1977) for rocks of central Massachusetts. Recent data on diffusion in garnet yield $D = 5.44 \times 10^{-21}$ m^2s^{-1} for T = 700°C (Chakraborty & Ganguly 1991).

Equation (1) may be applied to the garnet pod using a radius of 2 cm (2×10^{-2} m). This value of x represents the distance across the garnet pod in which individual grains of garnet are characterized by a steep compositional gradient (Fig. 8). This distance and calculation may be plausible if interconnecting networks of garnet grains provided a path or conduit for volume diffusion from the pod core to the surrounding pelitic schist. This may, in fact, be the case, because a continuous compositional gradient is recorded, for example, across adjacent grains 7 and 8 (Fig. 8). I argue that intragranular diffusion within garnet was dominant at high temperatures and that intergranular diffusion was volumetrically insignificant. Solution of equation (1) for a temperature of 700°C shows that homogenization of Fe–Mg zoning in the pod would be expected in approximately 62 Ma. Clearly, 62 Ma is a very long time for temperatures to remain at 700°C. Peak metamorphic conditions of 700°C probably only lasted 10 to 20 Ma (P. Robinson, pers. comm. 1991). Homogenization times calculated using the diffusion data of Chakraborty & Ganguly (1991) are several orders of magnitude greater and even more unreasonable. Calculations show, on the other hand, that if conditions were maintained at 750°C for 11 Ma, the pod could have completely homogenized. However, peak metamorphic temperatures calculated from surrounding schists and gneisses are typically around 700°C and not 750°C. Based on these simple calculations of rate of diffusion, the pod could not have homogenized at conditions of 700°C because the diffusion distance was too large.

This problem may be addressed further by considering the effects of intergranular diffusion, the probable presence of fluid during at least the early stages of metamorphism, and intragranular diffusion within individual garnet and surrounding matrix minerals. Such consideration should also take into account the relative rates of grain-boundary diffusion in relation to the relative rates of volume diffusion within garnet and matrix minerals. These considerations are used to develop a reasonable qualitative model of diffusion below.

In the early stages of metamorphism and garnet growth (garnet to staurolite grade), intergranular diffusion was probably the dominant diffusional mechanism, and may have been greatly enhanced by the presence of an intergranular fluid phase (Brady 1983). Garnet grains growing during this stage would be refractory compared to the matrix (Woodsworth 1977). As the grade of metamorphism and temperature increased, it is likely that the fluid phase was continually being driven off, and less refractory phases were becoming more and more able to homogenize constituents by volume diffusion. Volume diffusion within garnet itself would become important at temperatures above the sillimanite zone (Tracy 1982), and previously zoned grains of garnet would begin to homogenize. On the basis of the available analytical data, it appears that at some time during the history of the garnet pod, the relative rate of grain-boundary diffusion became approximately the same as the relative rate of volume diffusion both within individual grains of garnet and within matrix phases. This homogeneous volume-diffusion would allow, for example, movement of manganese away from the pod core into the surrounding layers both along grain boundaries and within garnet. Diffusing species such as Mn, Fe and Mg are more likely to move through garnet than through quartz or feldspar owing to crystal-chemical constraints. It was during this time that diffusional processes resulted in the formation of the presently observed compositional zoning in garnet grains from layers 2, 3 and 4/4a (Fig. 9). The already steep compositional gradient imposed on these layers by early diagenesis and sedimentation and later inter- and intragranular diffusion prevented the garnet grains from becoming homogeneous and resulted in the peculiar side-to-side zoning that they retain. Garnet grains in the pelitic schist (1) and the pod core (5), in contrast, could become homogeneous because they lay outside regions of steep compositional gradients at any time during their history.

Closely spaced electron-microprobe analyses of the rims of garnet grains from layers 2, 3 and 4/4a show no evidence of retrograde hydration reactions such as those described by Tracy (1975, 1978), Tracy *et al.* (1976) and Robinson *et al.* (1986). Such garnet is characterized by a homogeneous core and a continuous rim (Mn-rich) thought to have formed by continuous retrograde hydration reactions with matrix minerals in the presence of a fluid phase. The absence of such evidence in the garnet of this study suggests that prograde metamorphism drove away most of the metamorphic fluid or, in other words, that a fluid phase was unavailable for later retrograde reactions. Therefore, during the latest stages of metamorphism of the pod, there was a lack of intergranular fluid, and intragranular diffusional processes dominated.

DISCUSSION AND CONCLUSIONS

The sample investigated is mineralogically and chemically zoned and is characterized by individual grains of garnet that define sharp compositional differences across the pod. The high grade of metamorphism that affected this sample makes determination of the nature of its protolith difficult. However, geochemical evidence supports a model in which the protolith was a hydrogenous–diagenetic deposit unrelated to volcanogenic processes. In addition, the nature of the garnet-producing reactions is unknown; these were probably different in different parts of the pod. Diffusion at high temperatures removed garnet inhomogeneities in places such as the pelitic schist (1) and the pod core (5), but preserved compositional gradients in the intervening layers owing to compositional gradients already present. Simple calculations of rate of diffusion suggest that at least 62 Ma at 700°C would have been necessary to completely homogenize the garnet pod. This calculated length of time is too long for peak metamorphic conditions of 700°C to have been maintained, thereby preventing complete homogenization. Homogeneous volume-diffusion at some point during the history of the pod probably allowed the formation of the peculiar side-to-side zonation observed in garnet from the intervening layers 2, 3 and 4/4a. Intragranular diffusion appears to have been the dominant diffusional process during the late stages of regional metamorphism, allowing the preservation of a range of garnet compositions over a distance of 6 cm. What is clear from the extreme range of garnet compositions, is that the matrix was not very efficient in transporting material across this extreme gradient in chemical potential. Such inefficiency, even at 700°C, may well indicate a paucity of intergranular fluid in the pod in the late stages of regional metamorphism.

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