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Abstract. A large number of garnet phenocrysts from Palaeozoic rhyodacites and granodiorite porphyrites from Central and Northeastern Victoria have been analyzed using the electron microprobe. These garnets, from an area of several thousand square miles, are very uniform in composition (dominantly almandine, with subordinate pyrope and minor grossular and spessartine). They show minor zoning with a very thin outer rim slightly richer in almandine and spessartine than the remainder of the phenocryst. They are surrounded by a complex intergrowth of cordierite and hypersthene forming a reaction rim. Resorbed quartz phenocrysts are typically associated with the garnet phenocrysts. The uniform composition, the conspicuous size and the subhedral-euhedral form of the garnet phenocrysts indicate that they crystallized directly from the acid calc-alkaline magma at an early stage of its crystallization. High pressure experimental work on a natural garnet-bearing rhyodacite glass demonstrates that almandine-rich garnet and quartz are near-liquidus phases at 18 and 27 kb ( $P_{\rm HzO} < P_{\rm LOAD}$ ), but garnet does not appear until well below the liquidus at 9 kb. A comparison of the composition of the experimentally crystallized garnets with the natural garnets suggests that these acid calc-alkaline magmas began to crystallize at pressures between 9 and 18 kb, i.e. at depths corresponding to the lower crust or upper mantle.

# Introduction

Conspicuous almandine-rich garnet phenocrysts have been recorded in calcalkaline rocks from Victoria, Australia (EDWARDS, 1936; RINGWOOD, 1955), New Zealand (Cox, 1926), Japan (MIYASHIRO, 1955), England (OLIVER, 1956) and Russia (MAKAROV and SUPRYCHEV, 1964). Granodiorites, rhyodacites and dacites are the most common host rock-types for the garnet phenocrysts but they may also occur in rhyolites and andesites. MIYASHIRO (1955) pointed out that two garnet types are found associated with calc-alkaline rocks. These types are

- (i) garnets occurring as phenocrysts, and
- (ii) garnets occurring in cavities in lavas, or in pegmatites associated with calcalkaline plutonic rocks.

MIYASHIRO emphasized the compositional difference between these two types viz. garnets of the first type are almandine-rich with some pyrope and are poor in spessartine, while garnets of the second type are almandine-spessartine-rich and poor in pyrope. This paper is concerned with the origin of the phenocryst garnet type.

The garnet phenocrysts reach 2 cm in size and are subhedral-euhedral in form, showing varying degrees of reaction to a cordierite-hypersthene intergrowth in the case of the Victorian garnets or to a cordierite-biotite intergrowth (MIYASHIRO, 1955), or to a plagioclase intergrowth (OLIVER, 1956). They are typically associated with resorbed quartz phenocrysts (EDWARDS, 1936; Cox, 1926). Flow lines are present around some of the garnet phenocrysts (OLIVER, 1956). All these characteristic properties of the garnet phenocrysts occurring in calc-alkaline rocks point to the conclusion that the garnets initially crystallized directly from the

magma under equilibrium conditions at an early stage of crystallization, and later became unstable in their subsequent environment (EDWARDS, 1936; MIYASHIRO, 1955; OLIVER, 1956).

Recent high pressure experimental work investigating the origin of the calcalkaline igneous rock suite has indicated a means of deriving these rocks by partial melting of quartz eclogite at 100-150 kms depth (T. H. GREEN and RINGWOOD, 1966 and 1968), or by the wet partial melting  $(P_{\rm H,0} < P_{\rm LOAD})$  of basalt at 30-40 kms depth (T. H. GREEN and RINGWOOD, 1968). In the course of these investigations almandine-rich garnet was found to be the liquidus or near-liquidus phase (in association with quartz) in andesite and dacite compositions. These results demonstrate pressure-temperature conditions where early, equilibrium crystallization of acid calc-alkaline magma involved garnet and quartz. At lower pressures these phases are no longer present on or near the liquidus. Thus resorbed garnet and quartz phenocrysts observed in some calc-alkaline rocks may provide evidence of a deep origin of such magmas. The magmas began crystallization at depth where garnet and quartz are the near-liquidus phases, but on rising to shallower levels these phases are no longer in equilibrium with the host magma and began resorption and reaction to different phases, in equilibrium with the magma at lower pressure.

Accordingly to verify these interpretations of the occurrence and origin of garnet phenocrysts in calc-alkaline rocks, a two-fold investigation of the problem has been undertaken. This has involved:

(1) The determination of any characteristic compositional features of a large number of garnet phenocrysts, which may point to their igneous crystallization origin, or to an alternative hypothesis of origin (accidental inclusion of garnet xenocrysts in the calc-alkaline magma).

(2) A high pressure and high temperature study of the crystallization of a natural garnet-bearing rhyodacite<sup>1</sup> from Victoria, in order to determine the pressure-temperature stability field in which almandine-rich garnet may crystallize as a liquidus or near-liquidus phase (in association with quartz) from a rhyodacite magma.

#### Procedure

(1) The investigation of the natural garnets has involved many analyses using an electron microprobe (Applied Research Laboratories, EMX model). In the analytical techniques adopted chemically analyzed garnets have been used as standards. Since the garnet standards approximately cover the range of compositions of the garnets analyzed, no corrections have been made for absorption, atomic number or efficiency-of-generation factor (SMITH, 1966). Dead-time corrections are unnecessary for the count-rates used and background corrections are automatically allowed for in the calibration graphs prepared from the standard garnets. Fixed specimen current counting methods have been adopted. Using these techniques an estimated relative accurracy of 5% is obtained. Six elements (Fe, Mn, Mg, Ca, Ti and Al) have been analyzed. The silica content has been calculated using the determined cation contents, and assuming ideal garnet end-member compositions.

Electron microprobe traverses across garnet phenocrysts in four different polished thin sections have been conducted to determine the degree of zoning in the crystals, and also to determine the nature of the reaction rim around the garnet. Analyses of 9 different specimens

<sup>1</sup> Termed rhyodacite II in this paper, to distinguish this composition from the synthetic rhyodacite I (adamellite) used in other high pressure investigations (T. H. GREEN and RING-wood, 1968).

from a rhyodacite flow and 4 different specimens from a granodiorite have been conducted in order to determine the variability of garnet composition in a particular host rock. The specimens were prepared as grain mounts. Finally, analyses of 12 different garnets were obtained from different host rocks and localities spread over several thousand square miles in Victoria. The localities are summarized in Table 1. In order to determine whether there is any relation between host rock chemistry and the composition of the garnet, partial analyses of 7 host rocks have been conducted, and the garnet composition compared with the composition of the respective host rocks.

Table 1. Details of specimen localities from wh	hich the garnet-bearing calc-alkaline rocks were
obtained. The numbers refer to the catalogue in	the Department of Geophysics, A.N.U. Speci-
mens 2001, 2043-2047 were collected by one of	the authors (A.E.R.). Specimens 2048-2056
were supplied by Dr. I. McDougall	

Specimen Number	Rock name and details of location
2001, 2045-2047	granodiorite from Deddick
2043	quartz-biotite rhyodacite from Black Spur, 6 miles north-east of Heales- ville on the Healesville-Marysville Road
2044	quartz-biotite rhyodacite from 9.1 miles east of Marysville.
2048	rhyodacite from 5.65 miles east of Taggerty along the Blue Range Road
2049	rhy odacite from Lake Mountain Road Grid reference $878\mathrm{E},~735\mathrm{N}$ Juliet B , $840\mathrm{B}$ Zone $7$
2050	rhyodacite from Lake Mountain Road, 2 miles north of junction with Marysville-Woods Point Road
2051	rhyodacite from Lake Mountain Road, 1.3 miles from turnoff at Bellel
2052	rhyodacite from Black Spur on the Maroondah Highway between Dom Dom Saddle and Bladin's Quarry
2053	rhyodacite from near Toombullup, 3 miles from Holland's Creek Crossing
2054	granodiorite porphyrite 5 miles north of Tolmie on Mad House Road
2055	ring-dyke granodiorite porphyrite on Eildon-Jamieson Road south of Rocky Ridge, Jamieson Map Sheet 402.2 E, 390.3 N.
2056	ring-dyke granodiorite porphyrite from 300 yards east of 2055

(2) A natural garnet-bearing rhyodacite (rhyodacite II) from Victoria has been finely ground, melted and quenched to a glass. This glass has then been subjected to a series of experiments in a piston-cylinder high pressure and high temperature apparatus. The experimental techniques have been described in detail in other papers; a pressure correction of -10% has been applied (D. H. GREEN and RINGWOOD, 1967; T. H. GREEN, RINGWOOD and MAJOR, 1966). Approximately 20 mgm. of powdered rhyodacite II glass were packed into graphite sample capsules and about 1 mgm. of water added. Melting experiments have been conducted at 9, 13.5, 18 and 27 kb in order to determine the sequence of mineralogical changes, particularly the stability field of garnet, in the rhyodacite II composition with increasing pressure. The  $P_{\rm HsO}$  in the unsealed graphite capsules is not controlled, but is less than  $P_{\rm LOAD}$  and probably of the order of 2—5 kb. After the experimental runs the sample has been examined optically and by X-ray means, and where possible polished thin sections have been prepared to enable analysis of crystal phases (garnet) using the electron microprobe. The analytical techniques are similar to those described in the previous section.

#### Results

#### 1. Analyses of Natural Garnets

Electron microprobe traverses across a total of 11 garnet phenocrysts from 4 different polished thin sections revealed that the crystals are quite uniform in composition except for a marginal zone 10—40  $\mu$  wide which is slightly richer in almandine-spessartine and poorer in pyrope than the rest of the crystal. This is illustrated by the analyses of central and edge regions of garnets given in Table 2. Only one crystal does not show any zoning. The reaction rims around the garnets consist of iron-rich cordierite and hypersthene (e.g. approximate analysis: cordierite 8.4—9.6% FeO, 6.7—8.0% MgO; hypersthene 33.4—35.0% FeO, 12.1—14.1% MgO).

Table 2. Analyses of 4 garnet specimens prepared as polished thin sections in order to determine the amount of variation in composition across garnet crystals occurring in the Palaeozoic acid calc-alkaline igneous rocks of Victoria

Specimen	2043 (c) centre	2043 (c) edge	2043 (d) centre and edge (no difference)	2044 (a) centre	2044 (a) edge	2044 (d) centre	2044 (d) edge
No. of analyses	23	9	20	66	31	21	12
SiO.	38.4 a	38.1 a	38.6 ª	37.0 a	37.1 a	38.5 a	38.9ª
TiO,	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al.O.	21.7	21.5	21.8	21.7	21.6	21.7	21.5
FeO	32.35	33.2	32.5	31.2	32.2	33.3	35.0
MnO	$1.5_{5}$	1.8	1.5	1.6	2.5	1.3	2.5
MgO	5.55	4.8	5.6	5.2	4.3	5.3	3.9
CaO	1.7	1.6	1.7	1.6	1.6	1.7	1.6
will bedeted the	101.45	101.2	101.9	98.5	99.5	102.0	103.6
Mol. prop.		17	an en fra	The state	- cad		
Ti-And	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Gross	3.8	3.7	3.8	3.8	3.8	3.8	3.6
Pyrope	21.6	18.7	21.6	21.1	17.2	20.5	14.9
Alm	70.4	72.8	70.5	70.6	72.5	72.1	75.3
Spess	3.4	4.0	3.3	3.7	5.7	2.8	5.4
No. of different crystals analyzed in mount	2	2	1	6	6	2	2

<sup>a</sup> Denotes calculated content.

Analyses of 9 different specimens of garnet from one rhyodacite flow, and 4 different garnet specimens from a granodiorite are given in Tables 3 and 4 respectively. The garnets from the rhyodacite are quite uniform in composition, showing no more variation than the composition change observed from the centre to the edge of the crystals examined for zoning (see Table 2). Three of the four garnets from the granodiorite agree closely in composition, but the fourth is significantly different (2045). This fourth garnet occurred in the centre of a large ferromagnesianrich segregation (5 cms in size) in the granodiorite, while the other three garnets occurred as phenocrysts 0.2—1 cm in size surrounded by a ferromagnesian rim usually about 0.5 cms wide.

Analyses of 12 different garnets from different calc-alkaline host rocks from Victoria are given in Table 5. The specimens were obtained from localities up to 170 miles apart, covering an area of several thousand square miles. Examination

Specimen	(a)	(b)	(c)	(d)	(f)	(g)	(h)	(i)	(j)	Average
No. of analyses	10	10	32	20	10	10	10	12	10	124
SiO <sub>2</sub>	38.2ª	38.7 a	38.3 a	38.6 a	36.7 a	38.7 a	38.3 a	38.3 a	36.0 a	37.9 a
TiO <sub>2</sub>	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al <sub>2</sub> O <sub>3</sub>	21.5	22.1	21.6	21.8	21.8	22.0	22.0	22.2	21.6	21.3
FeO	33.0	33.9	32.6	32.5	31.0	33.7	32.6	32.7	30.4	32.6
MnO	2.4	1.4	1.6	1.5	2.4	1.8	1.5	2.0	1.3	1.8
MgO	4.6	5.0	5.3	5.6	4.7	4.8	5.3	5.1	5.2	5.1
CaO	1.6	1.7	1.6	1.7	1.7	1.7	1.7	1.6	1.6	1.7
<u>a</u> .	101.5	103.0	101.2	101.9	98.5	102.9	101.6	102.1	96.3	101.0
Mol. prop.										
Ti-And	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Gross	3.7	3.8	3.6	3.8	4.0	3.8	3.9	3.6	3.9	3.9
Pyrope	18.0	19.2	20.6	21.6	19.1	18.5	20.7	19.8	21.6	20.0
Alm	72.3	73.1	71.4	70.5	70.6	72.9	71.3	71.3	70.7	71.4
Spess	5.2	3.1	3.6	3.3	5.5	4.0	3.3	4.5	3.0	4.0

Table 3. Analyses of garnets from 9 different specimens all collected from one lava flow from Black Spur near Healesville, Victoria. Grain mounts were prepared to determine the variation in composition of garnet through one lava flow. Specimen numbers range from 2043 (a)-2043 (j)

<sup>a</sup> Denotes calculated content.

Table 4. Analyses of garnets from 4 different specimens all collected from the Deddick granodiorite. Grain mounts were used to check the variation in composition of garnet in the granodiorite

Specimen	2001	2045	2046	2047	Average
No. of analyses	10	10	16	10	46
SiO,	36.4 a	38.2 a	36.6 a	35.5 a	36.4 a
TiO,	0.2	0.2	0.2	0.2	0.2
Al <sub>2</sub> O <sub>3</sub>	21.8	21.4	21.8	21.4	21.6
FeO	32.1	35.1	32.8	30.8	32.7
MnO	2.1	3.7	1.3	2.3	2.3
MgO	4.2	2.9	4.4	4.0	3.9
CaO	1.4	1.4	1.4	1.7	1.5
	98.2	102.9	98.5	95.9	98.6
Mol. prop.					
Ti-And	0.6	0.8	0.8	0.8	0.8
Gross	3.5	3.1	3.3	4.0	3.5
Pyrope	17.2	11.2	18.0	21.1	15.9
Alm	73.8	76.7	74.9	69.3	74.5
Spess	4.9	8.2	3.0	4.8	5.3

<sup>a</sup> Denotes calculated content.

of Table 5 shows that with one exception (2053) these garnets are quite similar in composition. In order to compare the host rock chemistry with the garnet composition, partial analyses of 7 host rocks have been conducted. These are listed in Table 6 and it is evident from this table that the iron and magnesium contents of 6 of the host rocks are closely similar, but specimen 2053 is distinct. Because the chemistry of the host rocks is similar, apart from one case, little can be said about

Specimen	2043	2044	2048	2049	2050	2051	2052	2053	2054	2055	2056	Deddick average (from Table 4)
No. of analyses	124	87	15	12	16	15	6	16	24	10	10	46
SiO <sub>2</sub>	37.9 в	37.6 a	37.8 a	37.5a	37.4 <sup>a</sup>	36.8 a	38.4 a	36.4 a	37.7 a	35.5 a	36.7 a	36.4 a
TiO2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al <sub>9</sub> 0 <sub>8</sub>	21.8	21.7	21.9	21.7	21.6	21.6	21.8	21.5	21.7	21.4	21.6	21.6
FeO	32.5	32.2	31.5	32.3	31.9	32.0	32.3	37.2	32.4	29.4	30.1	32.7
0uM	1.8	1.5	1.4	1.6	1.6	1.9	1.5	1.5	1.7	1.8	1.2	2.3
MgO	5.1	5.2	5.7	5.0	5.0	4.5	5.5	2.0	5.0	5.1	5.7	3.9
CaO	1.7	1.6	1.7	1.6	1.8	1.6	1.8	1.0	1.7	1.7	1.9	1.5
adə ad bru bru bru	101.0	100.0	100.2	6.99	99.5	98.6	101.5	8.66	102.9	95.1	97.4	98.6
Mol. prop.	(8)	51. 19 4	0		19 19 19	1. N.	in i isa	1. J. B. B.	18.0	1.1.1	140.	
Ti-And	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Gross	3.9	3.7	3.9	3.7	4.3	3.8	4.2	2.0	3.9	4.2	4.7	3.5
Pyrope	20.0	20.7	22.5	19.8	19.9	18.2	21.3	8.2	19.7	21.4	23.1	15.9
Alm	71.4	71.4	69.69	72.0	71.3	72.8	70.4	85.5	71.8	69.3	68.6	74.5
Spess	4.0	3.4	3.2	3.7	3.7	4.4	3.3	3.5	3.8	4.3	2.8	5.3
<sup>a</sup> Denotes calcu	lated cont	tent.				1001	10	2 1 221	20.00	P D L	2000	

T. H. GREEN and A. E. RINGWOOD:

any relation between the host rock chemistry and the garnet composition, except that it is significant to note that the one exceptional garnet composition (2053) of Table 5 occurs in the one exceptional host rock composition of Table 6, and the MgO ratio of the garnet FeO follows that of the host rock. This suggests, but does not prove, a link between the host rock composition and the garnet composition.

2. High Pressure Investigation of a Natural Garnet-Bearing Rhyodacite II Composition

The results of the high pressure runs are summarized in Table 7.

Three runs at 9 kb have been conducted. At 820°C, well below the liquidus, the phases present are quartz, plagioclase, amphibole, mica and rare garnet. Two runs conducted at 840° C show different degrees of crystallization reflecting the possible variation in  $P_{\rm H,O}$  in the experimental procedure adopted for these wet runs. The phases present in the run showing a greater degree of crystallization are quartz, plagioclase, mica and uncertain amphibole and clinopyroxene. In the second run plagioclase and amphibole are the only phases present. This run serves the purpose of illustrating the nature of the

168

Specimen	2043	2044	2048	2053	2054	2056	2001
Al <sub>2</sub> O <sub>3</sub>	16.1	15.7	15.4	15.8	17.6	17.0	14.7
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.8	0.55	0.4	0.9	0.5	1.0
FeO	3.6	3.8	3.6	2.1	3.9	3.35	3.5
MnO	n.d.ª	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	1.5	1.5	1.4	0.5	1.7	1.3	1.6
CaO	3.2	3.2	3.0	1.9	3.6	2.8	1.5

Table 6. Partial analyses of glasses prepared by melting natural garnet-bearing calc-alkaline rocks from Victoria. FeO,  $Fe_2O_3$  determinations by chemical methods have been conducted by E. KISS, A.N.U., on the natural rock powder prior to melting. Other determinations were obtained using the electron microprobe

<sup>a</sup> Not detected above background using electron microprobe techniques.

near-liquidus phases in the rhyodacite II at 9 kb. Garnet is not present in either of the runs at 840°C but it does occur in the run at 820°C which shows the greatest degree of crystallization. Thus garnet is not a near-liquidus phase at 9 kb.

Two runs have been conducted at 13.5 kb. At  $910^{\circ}$ C quartz and plagioclase are the main phases, with minor mica, garnet and amphibole, while at  $870^{\circ}$ C clinopyroxene was identified as well. No reliable analyses of the garnet crystals were obtained because of the presence of abundant inclusions.

At 18 kb garnet is the near-liquidus phase in a run at 920°C, and it is joined by quartz and possibly clinopyroxene at 890°C, while at 840°C large crystals of garnet and quartz occur, together with minor blue pleochroic amphibole (glaucophane ?). At 800°C near the solidus mica, plagioclase, amphibole and quartz are present, but no garnet or clinopyroxene was identified. Microprobe analyses of the garnets were obtained.

One run on the rhyodacite II composition was conducted at 27 kb. No water was added to this run, so that the liquidus has not been lowered substantially (compared with the runs from 9—18 kb). Garnet (suitable for microprobe analysis) and quartz were the phases crystallizing at  $1340^{\circ}$ C in this run.

Analyses of garnets from these experimental runs are given in Table 8. Because of the rarity of garnet at 9 kb only one crystal could be analyzed. This proved to be very almandine rich, with minor spessartine, grossular and pyrope. At 18 kb several garnets were analyzed from runs showing different degrees of crystallization. These garnets are almandine-rich with subordinate pyrope, grossular and minor spessartine. With increasing degree of crystallization the almandine and grossular contents increase, while the pyrope content decreases. The garnet at 27 kb is similar in composition to the garnets from the runs at 18 kb showing a low degree of crystallization.

### **Interpretation of Results**

Several results from the study of the composition and petrography of garnet phenocrysts in the Victorian calc-alkaline rocks point to their igneous crystallization origin at depth, over a limited pressure-temperature range, rather than their

12 Contr. Mineral. and Petrol., Vol. 18

Phases	Present		and contracts		and the set	a shiraran	Estimated % of Glass	Comments and estimat crystal phases present
mica <sup>a</sup>	amph		plag	qz	ga	glass	60	Rare large euhedral ga and plagioclase, anh mica≫ ga
mica <sup>a</sup>	amph ?	cpx ?	plag	qz		glass	70	Common quartz, plagic tification of amphib garnet; $qz > plag$ , m
	amph		plag			glass	90	Minor acicular plagioo plag>amph
mica <sup>a</sup>	amph ?	cpx	plag	qz	ga	glass	50	Fine grained except for uncertain identificat cpx>mica>ga, am
mica <sup>a</sup>	amph		plag	qz	ga	glass	70	As above except no cl phibole definitely pr
mica <sup>a</sup>	amph		plag	$\mathbf{q}\mathbf{z}$		glass	?	Fine grained, near-soli identified; $qz > amp$
	amph			qz	ga	glass	70	Common large euhedra blue amphibole prism
					ga	glass	96	Large, euhedral garnet
		cpx ?		qz	ga	glass	80	Well crystallized garn crystals of clinopyro:
					ga	glass	98	Large, clear euhedral g
						glass	100	Above liquidus
	T ally		- Biller	qz	ga	glass	85	Large, inclusion-bearing qz>ga

mental runs on the rhyodacite II composition under wet conditions

by X-ray means alone. <sup>b</sup> No water added to this sample, pyrophyllite spacer dried.

Conditions of run	27 kb 1340°C 80 mins <sup>b</sup>	18 kb 920°C 150 mins	18 kb 880°C 240 mins	18 kb 890°C 180 mins	18 kb 840°C 240 mins	9 kb 820°C 255 mins
Co-existing phases	qz	-	-	qz, cpx ?	qz, amph	qz, amph, plag, mica
SiO <sub>2</sub>	35.0 a	37.2 a	37.9 a	36.3 a	37.1 a	36.8 a
$TiO_2$ Al <sub>2</sub> O <sub>3</sub>	1.0 $21.9$	1.6 $21.6$	1.4 $20.7$	1.8 $21.9$	1.4 $21.0$	20.8 a
FeO	28.1	25.0	24.9	22.2	26.7	38.0
MnO	0.2	0.6	0.6	0.4	0.9	1.0 a
MgO	4.5	7.4	5.9	5.2	4.1	1.0
CaO	4.4	4.4	6.5	9.0	7.4	2.4
	95.1	97.8	97.1	96.8	98.6	100.0
$\frac{100 \text{ Mg}}{\text{Mg} + \text{Fe}}$	22.2	34.5	29.7	29.4	21.5	4.4
Mol. prop.						
Ti-andracite	3.2	4.7	4.4	5.5	4.4	
grossularite	10.0	8.1	14.4	20.9	17.0	7.1
pyrope	19.2	29.6	23.7	21.4	16.4	4.0
almandine	67.1	56.2	56.1	51.3	60.1	86.5
spessartine	0.5	1.4	1.4	0.9	2.1	2.4

Table 8. Electron microbe analyses of garnets crystallizing from the rhyodacite II composition at high pressures. Runs conducted under wet conditions (1 mgm  $H_2O$  added) in graphite capsules

 $\rm Fe_2O_3$  content cannot be determined using the electron microprobe, so the total iron content has been calculated as almandine. Since the runs were conducted in graphite capsules, reducing conditions results so that the  $\rm Fe_2O_3$  content is small or absent and neglect of any andradite component should not be serious.

<sup>a</sup> Denotes calculated content.

12\*

<sup>b</sup> No water added to this sample.

accidental inclusion as xenocrysts in the calc-alkaline magma. These features may be summarized as follows:

(i) The garnets exhibit large size (up to 1 cm), subhedral-euhedral habit and are free of inclusions. In contrast, almandine garnets from metamorphic environments typically contain abundant inclusions (ATHERTON and EDMUNDS, 1966; T. H. GREEN, 1966, 1967).

(ii) The natural garnets are characterized by an extremely uniform composition even though they come from different host rocks spread over an area of several thousand square miles.

(iii) There is a possible direct relation between the garnet composition and the composition of the host rock.

(iv) Minor zoning (rims slightly richer in Fe, Mn and poorer in Mg than the cores) which occurs in the garnet phenocrysts is consistent with the zoning expected during igneous crystallization. The zoning always followed this consistent pattern. No other variations or reverse zoning was observed as might be expected if the garnets were xenocrystal in origin, derived by accidental inclusion from a meta-morphic terrain (e.g. garnets from metamorphic terrains studied by ATHERTON and EDMUNDS, 1966; BANNO, 1965 exhibited marked zoning; however almandine

garnets from some high grade metamorphic rocks from Australia showed no zoning, T. H. GREEN, 1967).

(v) Experimental evidence has shown that almandine-rich garnets are a liquidus or near-liquidus phase crystallizing from rhyodacite at >9 kb under conditions of  $P_{\rm H_{2}O} < P_{\rm LOAD}$ . Thus for these conditions almandine-rich garnet may crystallize directly from an acid calc-alkaline magma.

(vi) The garnet phenocrysts are unstable at near-surface conditions, and react with the rhyodacite liquid to form cordierite-hypersthene rims. This cordierite-



hypersthene association is typical of low pressure, high temperature metamorphic conditions (TURNER and VERHOOGEN, 1960).

As indicated in point (v) above the high pressure experimental work on the rhyodacite composition broadly supports the igneous crystallization origin of the almandine-rich garnets at great depth. However a comparison of the experimental and natural garnet compositions shows that the near-liquidus garnets crystallizing at 18 and 27 kb are significantly richer in grossular and poorer in almandine than the natural examples. The garnet crystallizing at 9 kb, 840°C in company with

quartz, plagioclase and mica, has a grossular content comparable with the natural garnets, but the almandine content is high and the pyrope content is low when compared with the natural garnets. This is illustrated in Fig. 1, where triangular plots of the garnet end members of the natural and experimental garnets are given.

Thus the major discrepancy in composition is the higher grossular content in the garnet obtained experimentally when compared with the natural garnets. It is important to note that the compositions of the garnets crystallizing at 18 kb showed a decrease in grossular content with decreasing degree of crystallization. The grossular content of the garnet well below the solidus is significantly higher where garnet crystallizes in conjunction with other calcium-bearing phases (e.g. clinopyroxene or amphibole). Also there is a probable trend of increasing grossular content with increasing pressure, for constant degrees of crystallization (as observed in other calc-alkaline compositions at high pressure, T. H. GREEN and RINGWOOD (1968). At 9 kb the rare garnet observed occurs well below the liquidus and it is not a near-liquidus phase. Hence at some pressure less than 18 kb but greater than 9 kb, garnets with composition corresponding to the natural garnets (particularly in grossular content) will probably form on the liquidus of the rhyodacite II composition.

# Conclusions

From this study of natural garnet phenocrysts in calc-alkaline rocks of Victoria, we conclude that these garnets crystallized directly from the calc-alkaline magma at an early stage of its crystallization, then at a later stage became out of equilibrium with the magma and began to react to cordierite and hyperstheme. The experimental investigation of the stability and composition of almandine-rich garnet occurring as a liquidus phase in the natural rhyodacite at high pressure demonstrates that garnets with the same composition as the natural garnets, may in fact crystallize from the rhyodacite as a near-liquidus phase at pressures greater than 9 kb but less than 18 kb, for conditions of  $P_{\rm H_{s}0} < P_{\rm LOAD}$ . These results support the interpretation that the garnet phenocrysts represent early crystallization of rhyodacite magma at great depth (e.g. at the base of the crust or in the upper mantle). The cordierite-hyperstheme reaction rim represents a low pressure-high temperature equilibrium assemblage.

The liquidus temperature and nature of the liquidus phase will be governed to an important degree by the  $P_{\rm H_{2}O}$ . In a relatively dry magma ( $P_{\rm H_{4}O} \ll P_{\rm LOAD}$ ) the liquidus temperature will be higher, and a higher pressure will be necessary to obtain garnet as a near-liquidus phase. In such cases, near-liquidus garnet phenocrysts will only form at mantle depths, even in continental areas. This may well be true for the Victorian calc-alkaline garnet-bearing rocks, since HILLS (1959) believed that the magmas were relatively dry and must have commenced crystalization at a high temperature. The reverse will hold true for a very wet magma and garnet may then form at lower crustal pressures. If the magma has a high  $P_{\rm H_{2}O}$  amphibole, not garnet, may appear on the liquidus. Thus for any particular acid calc-alkaline composition there is a limited range of pressure and temperature (depending on the  $P_{\rm H_{2}O}$ ) over which garnet may form as a near-liquidus phase.

174 T. H. GREEN and A. E. RINGWOOD: Origin of Garnet Phenocrysts in Calc-Alkaline Rocks

#### References

ATHERTON, M. P., and W. M. EDMUNDS: An electron microprobe study of some zoned garnets from metamorphic rocks. Earth and Planetary Sci. Letters 1, 185–193 (1966).

BANNO, S.: Notes on rock-forming minerals: zonal structure of pyralspite garnet in Sanbagawa Schists in the Bessi area, Sikoku. J. Geol. Soc. Japan 71, 185–188 (1965).

Cox, P. T.: Geology of the Rakaia George district. Trans. Proc. New Zealand Inst. 56, 91-111 (1926).

EDWARDS, A. B.: On the occurrence of almandine garnets in some Devonian igneous rocks of Victoria. Proc. Roy. Soc. Victoria 49, 40-50 (1936).

GREEN, D. H., and A. E. RINGWOOD: An experimental investigation of the gabbro to eclogite transformation and its petrological applications. Geochim. et Cosmochim. Acta 31, 767– 833 (1967).

GREEN, T. H.: Thermal metamorphism in the Trial Harbour district, Tasmania. J. Geol. Soc. Australia 13, 405-418 (1966).

- High pressure experimental investigations on the origin of high-alumina basalt, andesite and anorthosite. Aust. Nat. Univ., Unpubl. Ph. D. Thesis (1967).
- ---, and A. E. RINGWOOD: Origin of the calc-alkaline igneous rock suite. Earth and Planetary Sci. Letters 1, 307-316 (1966).
  - — Genesis of the calc-alkaline igneous rock suite. Contr. Mineral. and Petrol. 18, 105—162 (1968).
- ---, and A. MAJOR: Friction effects and pressure calibration in a piston-cylinder apparatus at high pressure and temperature. J. Geophys. Research 71, 3589-3594 (1966).

HILLS, E. S.: Cauldron subsidences, granitic rocks and crustal fracturing in S. E. Australia. Geol. Rundschau 47, 543 (1959).

MAKAROV, N. N., and V. A. SUPRYCHEV: Xenogenic garnet (pyrope-almandine) from volcanic rocks of the Crimea. Doklady Akad. Nauk S.S.R. (Engl. Transl.) 157, 64—67 (1964).

MIYASHIRO, A.: Pyralspite garnets in volcanic rocks. J. Geol. Soc. Japan 61, 463—470 (1955). OLIVER, R. L.: The origin of garnets in the Borrowdale Volcanic series and associated rocks,

English Lake District. Geol. Mag. 93, 121-139 (1956).

RINGWOOD, A. E.: Geology of the Deddick-Wulgulmerang area, East Gippsland. Proc. Roy. Soc. Victoria 67, 19-66 (1955).

SMITH, J. V.: X-ray-emission microanalysis of rock-forming minerals. I. Experimental techniques. J. Geol. 73, 830-864 (1965).

TURNER, F. J., and J. VERHOOGEN: Igneous and metamorphic petrology. New York: McGraw-Hill Book Co. 1960.

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