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Constraints on the origin of mantle-derived low Ca garnets

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Abstract. Current hypotheses for the source rock of low Ca garnets hosted in mantle-derived diamonds and xenoliths range from residues of komatiite generation, to subducted serpentinite, to subducted mid-ocean ridge (MORB) harzburgite. Experiments designed to test these hypotheses were undertaken. The stability and compositional variation of garnets at pressures above 4 GPa through the melting interval of hydrous peridotite, in the subsolidus of depleted harzburgite and peridotite compositions, and along the liquidus of aluminium-undepleted and aluminium-depleted komatiites were examined, and compared with petrological data for natural low Ca garnets. Partitioning of Cr between garnet and ultramafic liquid along the liquidus of komatiites and within the melting interval of peridotite, indicates that garnets in mantle residues after single stage Archean ultramafic liquid removal would contain 2 to 4 wt% Cr_2O_3. Thus, the more Cr-poor population of mantle-derived low Ca garnets, with Cr_2O_3 less than 4 wt%, could have originated by such a process. Experimental results for other compositions indicate that average cratonic peridotite or its hydrated equivalent is typically too Cr-poor to be the protolith from which low Ca garnets containing greater than 4 wt% Cr_2O_3 could have crystallized in the upper mantle. Experiments on a spinel harzburgite composition indicate that an extremely Cr-rich protolith ($Cr/Cr + Al > 0.3$) is required to crystallize spinel and Cr-rich low Ca garnets, at pressures deduced for the ultramafic inclusion suite in diamonds (5 to 7 GPa). Natural examples of such Cr-rich protoliths are represented in some ophiolite harzburgites. All the experimental data taken together require that low Ca garnets with greater than 4 wt% Cr_2O_3 originated from residues that underwent multiple melt extraction. Whether such multi-stage events formed protoliths for low Ca garnets at shallow (i.e. MORB source region) or deep (i.e. komatiite source region) levels in the Precambrian mantle is not completely resolvable. The former environment can better account for the abundance of spinel in many diamonds hosting low Ca garnets, but the latter scenario best explains the presence of low Ca garnets in harzburgite xenoliths with 'cratonic' bulk compositions well removed from typical MORB residues.

Introduction

Garnets rich in Cr_2O_3 and MgO, and poor in CaO, occur as inclusions in diamonds, as xenocrysts, or as constituent minerals of rare harzburgite and dunite xenoliths, hosted in kimberlites erupted within Archean cratons (Sobolev et al. 1973; Gurney and Switzer 1973; Nixon et al. 1987). Because low Ca garnets commonly occur dispersed in kimberlite erupted within Archean cratons (Boyd and Gurney 1982), or as inclusions in diamonds of Precambrian age, there has been much interest in their use as a probe for characterizing the processes leading to the development of ancient continental lithosphere, and the conditions under which diamonds form in the upper mantle.

The characteristic 'low Ca' signature of mantle-derived garnets is based mainly on their disposition in a CaO vs Cr_2O_3 plot. Garnets saturated with diopside and therefore with Ca, plot within a field defined by numerous analyses of lherzolite garnets (Sobolev 1974) whereas those which are sub-calcic or Ca-undersaturated, plot outside the boundary for lherzolites (Fig. 1). Most low Ca garnets are thought to have equilibrated in a diopside-free lithology in the upper mantle (Sobolev 1974). The high Mg and Cr contents of many low Ca garnets, particularly those included in diamond (Gurney et al. 1979), indicate a source rock for low Ca garnets that is rich in MgO and Cr_2O_3 and thus more depleted than most peridotite sampled in kimberlites and alkaline lavas, or in oceanic crust and ophiolites.

There have been three main theses advanced regarding the origin of low Ca garnets. Boyd and Gurney (1982) first noted that low Ca garnets (and diamonds) may occur in kimberlites erupted within Archean cratons, but are suspiciously absent in 'off-craton' kimberlites. Based on this

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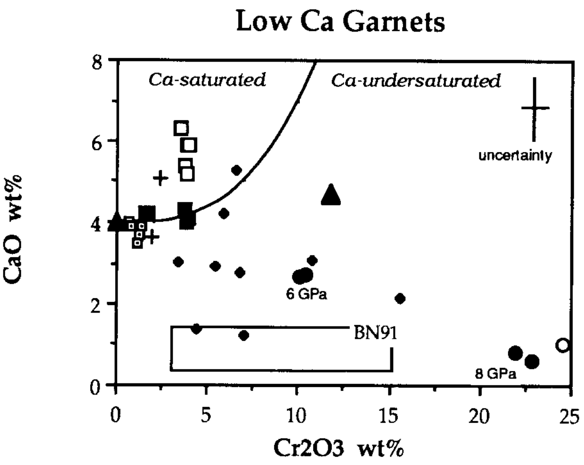

Fig. 1. CaO vs Cr_2O_3 plot for garnets. The *curved line* distinguishes garnets which are Ca-saturated (above the line) from those which sub-calcic or Ca-undersaturated (below the line). *Diamonds*, garnets included in diamonds (Gurney et al. 1979); the *boxed field* labelled BN91 is a population maximum for garnets included in diamonds adapted from Gurney's data in Boyd et al. (submitted). *Squares with dots*, garnets crystallized along the liquidus of aluminium-depleted and aluminium-undepleted komatiites; most of these garnets are considered to be mildly subcalcic in composition. *Crosses*, garnets crystallized within the melting interval of peridotite at 3 (calcic), 5 and 14 GPa (barely subcalcic) (data from Takahashi 1986). *Filled squares*, garnets crystallized from cratonic peridotite KAP1 at 5 GPa-1450 °C, 6 and 8 GPa-1600 °C; these garnets are all also marginally sub-calcic. *Open squares*, garnets crystallized from cratonic peridotite KAP1 at temperatures less than 1450 °C (5–8 GPa). *Filled triangles*, garnets crystallized from a harzburgite-liquid assemblage for composition V25 (no Cr) and V25 + Cr (filled). *Circles*, garnets crystallized from spinel harzburgite SHZ1 at 1400 (filled) and 1600 °C (open) with pressures labelled. All data are given in Table 3

observation, they proposed that such garnets have originated during deep seated melting events leading to komatiite generation in the Archean, the residues of which are represented by rare harzburgite xenoliths containing low Ca garnets. These harzburgites have bulk compositions with 'cratonic' affinity, well removed from typical MORB residues (Boyd et al. submitted), and are thought to be intermixed with garnet lherzolite within the Kaapvaal craton of southern Africa (Nixon et al. 1987; Boyd 1989). That garnet was a likely residual phase in komatiite generation at high pressures has long been debated (Nesbitt et al. 1979; Beswick 1982; Ohtani 1984) but is evidenced most recently by Lu-Hf isotopic (Gruau et al. 1990) and phase equilibrium studies of komatiites (Wei et al. 1990; Trønnes et al. in press).

Schulze (1986) suggested that ocean floor serpentinite, being rich in Mg and poor in Ca, is a suitable lithology from which Mg-rich and Ca-poor garnets can crystallize, once metamorphosed to its high pressure and temperature equivalent by subduction. Schulze (1986) proposed that low Ca garnets and associated refractory olivine, orthopyroxene or spinel in south African diamonds could have crystallized from serpentinite protoliths subducted and later accreted to the Archean Kaapvaal craton of southern Africa.

In essence, a similar origin for low Ca garnets was proposed earlier by Ringwood (1977) and later amplified in Kesson and Ringwood (1989). Their model also assumes original depletion of the low Ca garnet protolith in the mid-ocean ridge environment. In this model, harzburgites enriched in Mg and depleted in Ca are formed by repeated melt extraction at mid-ocean ridges and, once subducted to high pressures, crystallize refractory low Ca garnets, olivine, spinel and orthopyroxene. These subducted harzburgites are thought to have been accreted to the mantle roots of Archean cratons. Diamonds which crystallized within this accreted harzburgite lithosphere (containing inclusions of refractory olivine, orthopyroxene, spinel, and low Ca garnet) were later entrained in kimberlite magmas.

In this study, the stability and compositional variation of garnets crystallized at pressures above 4 GPa in various bulk compositions in synthetic and natural systems are examined and used to test current hypotheses described above for the origin of low Ca garnets. The results provide further constraints on the nature of the protolith and conditions of formation for these peculiar garnets.

Experimental approach and methods

Experiments were designed to test either directly or indirectly each proposal described above for the origin of low Ca garnets. Except where noted, all experiments were performed at the Bayerisches Geoinstitüt with a multianvil apparatus (Sumitomo 1200) using Toshiba F grade WC cubes having an 11 mm truncated edge length for pressure generation, and 18 mm edged Cr_3O_3 doped MgO octahedra as pressure media. Pressure was calibrated at room temperature using transitions in Bi (I–II, III–V) and at 1000 °C and 1450 °C using the quartz-coesite, coesite-stishovite and fayalite-γ-spinel transitions as fixed points (Böhlen 1984; Yagi and Akimoto 1976; Yagi et al. 1987, respectively). Pressures are accurate to ± 0.3 GPa based on the width of these reversal brackets. Temperatures were measured with $Pt\text{-}Pt_{90}Rh_{10}$ or $W_{75}Re_{25}\text{-}W_{97}Re_3$ thermocouples inserted axially in assemblies with sectioned graphite heaters having a thermal gradient of less than 20 °C/mm across the sample capsule. Temperatures were uncorrected for pressure effects on thermocouple EMF. Temperature was controlled within ± 2 °C of the set point, but in some experiments, thermocouples were lost during heating. In these latter experiments, temperature was estimated from power to the furnace assembly, and is accurate to ± 25 °C.

Electron microprobe analyses of all run products were performed at the Bayerisches Geoinstitüt with a Cameca Camebax SX50 instrument in the wavelength dispersive mode, using an accelerating voltage of 15 kV, probe current of 15 nA, and counting times of 20s on peaks. Diopside (Ca), enstatite (Mg), Cr_2O_3 (Cr), andradite (Fe), spinel (Al), and orthoclase (Si) were employed as standards, and four to eight points for each phase in each run product were analysed. Data were reduced with a ZAF procedure.

Low Ca garnets as residues of Archean komatiite formation

If this hypothesis (Boyd and Gurney 1982) for the origin of low Ca garnets were correct, garnets crystallized at high pressure along the liquidus of ultramafic liquids, above the peridotite solidus, or within the subsolidus of cratonic peridotite bulk compositions, should have compositions not unlike those of mantle-derived low Ca garnets.

As an experimental test of this proposal, garnet compositions along the liquidus of an aluminium depleted komatiite and an aluminium undepleted komatiite were examined and compared with those of natural low Ca garnets. The experiments that provide these data are reported by Wei et al. (1990) and were performed at the University of Alberta (Table 1). The electron microprobe analyses of both coexisting garnets and quenched liquid from the komatiite liquidus experiments (Trønnes et al. (in press), were combined with available data on the melting of peridotite at high pressures (Takahashi 1986) and were used to derive partition coefficients for Cr between garnet and ultramafic liquid. These partition coefficients constrain the amount of Cr partitioned into garnets in residues of ultramafic melt removal.

Harzburgite xenoliths with 'cratonic' bulk compositions, and which host low Ca garnets, are also thought to be the residues of Archean ultramafic liquid extraction (Nixon et al. 1987; Boyd et al. submitted). To test this particular idea, garnets crystallized in phase equilibrium experiments undertaken on a 'cratonic' peridotite bulk composition (see Boyd 1989), were compared with naturally occurring low Ca garnets. The latter experiments were performed on an average 'cratonic' peridotite composition (KAP1) in the system $CaO–MgO–Al_2O_3–SiO_2–FeO–Cr_2O_3$ (Table 1). An oxide mix of KAP1 was ground under alcohol, dried, and heated to 1600 °C in a Pt crucible at 101 kPa (1 atm) in air for 3 hours to form a starting material consisting of olivine and glass. At 101 kPa in air negligible iron loss occurs from Fe-bearing melts to platinum crucibles due to the low solubility of Fe in Pt metal under such oxidizing conditions. This material was then ground to less than 5 μm and stored over desiccant. Experiments on the KAP1 starting material employed graphite capsules and were run at 5 to 8 GPa and 1300–1600 °C for 1 to 11 h (Table 2). The interpretation of phase relationships for cratonic peridotite KAP1 (Table 2) is the subject of a separate study (Canil, 1991).

Low Ca garnets crystallized from a subducted serpentinite protolith

To test this theory (Schulze 1986), garnets crystallized from a garnet harzburgite assemblage within the melting interval of a synthetic peridotite in the system $CaO–MgO–Al_2O_3–SiO_2–CO_2–H_2O$ at 6 GPa were analysed and compared with those of naturally occurring low Ca garnets. The synthetic peridotite (V25, Table 1) is a mixture of reagent grade MgO, SiO_2, Dora Maira garnet, Iceland spar calcite, and pure brucite (99.98% Johnson-Mathey). This mixture was ground under alcohol to a grain size of 10 μm, dried and stored over desiccant. In one experiment, 2 wt% Cr_2O_3 was added and mixed into V25 (V25 + Cr, Table 1). Approximately 5 to 10 mg of V25 was loaded in 2 mm diameter Pt capsules and sealed by arc welding. These capsules were run at temperatures of 850 to 1150 °C for 15 to 20 h, using procedures described above. At 6 GPa and 1075 °C, V25 and V25 + Cr crystallize a garnet harzburgite + liquid assemblage (Table 2). Garnets from these latter experiments are assumed to represent those of a depleted serpentinite composition metamorphosed by subduction to a harzburgite assemblage at similar P-T conditions (i.e. 1075 °C, 6 GPa).

Low Ca garnets crystallized from subducted mid-ocean ridge harzburgite

To examine this hypothesis (Kesson and Ringwood 1989), phase equilibrium experiments were performed at 1200 to 1600 °C from 5 to 8 GPa on a synthetic spinel harzburgite composition (SHZ1, Table 1). Spinel harzburgite SHZ1 is composed of natural olivine and orthopyroxene from a large spinel lherzolite xenolith (sample JL-1, Canil et al. 1990) and synthetic picrochromite, mixed in weight proportions of 6 : 3 : 1 and ground under alcohol to a grain size of less than 10 μm. The extremely high Cr content of SHZ1 (Table 1) was intended to highlight the problem in defining suitable protoliths for extremely Cr-rich garnets in diamonds, as is discussed later. The procedures for experiments on SHZ1 are identical to those described above for peridotite composition KAP1.

Equilibrium and reversal of garnet composition

Equilibrium was assumed based on various observations. Firstly, experiments designed to test the stable equilibrium phase assemblage were performed under 'worst case' conditions (1300 °C, 5 GPa Table 2) by bringing the experiment to higher temperature (1525 °C) for 2 h to crystallize phases stable at that temperature and then lowering the temperature to 1300 °C for 9 to 11 h to approach the phase assemblage at 1300 °C from higher temperature. These experiments (e.g Run 292, Table 2) produced phase assemblages identical to those observed in a typical experiment where the run is simply pressurized and then heated to 1300 °C (e.g. Run 273, Table 2).

Secondly, the compositional overlap of garnets synthesized in three different experiments at the same 'worst case' run conditions (i.e. 5 GPa, 1300 °C), approached from both high (Runs 305, 292)

Table 1. Starting materials

Sample	M620[a]	HSS15[a]	SHZ1	KAP1	V25	V25 + Cr	AB1
SiO_2	45.6	46.77	41.64	46.57	43.37	42.51	43.75
TiO_2	0.40	0.33					
Al_2O_3	7.95	3.42	1.21	1.46	3.03	2.97	1.18
Cr_2O_3	0.16	0.20	7.31	0.40		2.0	0.20
FeO*	12.66	11.26	7.62	6.24			8.31
MnO	0.20	0.19					
MgO	25.00	31.51	42.45	44.05	37.75	37.00	45.41
CaO	7.60	5.67	0.18	0.79	2.80	2.74	1.14
CO_2					2.20	2.17	
H_2O					10.85	10.63	
Total	99.57	99.35	100.41	99.06	100.00	100.00	100.00
Mg/(Mg + Fe)[b]	0.732	0.795	0.885	0.907			0.883
Cr/(Cr + Al)[b]	0.017	0.048	0.840	0.19		0.37	0.13
Ca/Al[c]	1.29	2.23	0.20	0.73	1.25	1.25	1.31
Mg/Si[c]	0.71	0.87	1.32	1.22	1.12	1.12	1.34
Composition	AUK	ADK	Sp-Hz	Per	Per	Per	Per

[a] Details of analysis and preparation given in Wei et al (1990)
[b] atom fraction
[c] weight fraction
FeO* all Fe as FeO
Sp-Hz, spinel harzburgite; Per, peridotite; AUK, aluminium undepleted komatiite; ADK, aluminium depleted komatiite

Table 2. Experimental conditions

Sample	Run#	T(°C)	P(GPa)	Time[c]	Results
M620					
	569	1800	5.7	5	gt + l
	168	1800	6.0	10	gt + opx + l
	247	1860	10	5	gt + l
HSS15					
	242	1900	12	5	gt + l
KAP1					
	312	1600	5	2	ol + opx
	272	1525	5	2	ol + opx
	263	1450	5	6	ol + opx + gt
	306	1400	5	8	ol + opx + gt
	273	1300	5	10.5	ol + opx + gt
	292	1300	5	11	ol + opx + gt[a]
	305	1300	5	9	ol + opx + gt[a]
	386	1450	5.5	7	ol + opx + gt[b]
	217	1600	6	2	ol + opx + gt
	286	1450	6	9	ol + opx + gt
	276	1450	7	6	ol + opx + gt
	216	1600	8	2	ol + opx + gt
^{57}Fe-Py					
	294	1300	7	8	gt
V25					
	131	850	6	20	ol + opx + cpx + gt + cm + h
	223	925	6	15	ol + opx + cpx + gt + cm + h
	128	1000	6	19	ol + opx + cpx + gt + l
	184	1075	6	15	ol + opx + gt + l
	380	1075	6	20	ol + opx + gt + l
	108	1150	6	16	ol + opx + l
V25 + Cr					
	381	1075	6	20	ol + opx + gt + l
SHZ1	372	1200	5	29	ol + opx + sp
	156	1400	6	7	ol + opx + gt + sp
	180	1400	8	6	ol + opx + gt + sp
	306	1400	5	8	ol + opx + sp
	386	1450	5.5	7	ol + opx + gt
	208	1600	5	1.5	ol + opx + sp
	207	1600	6	1	ol + opx + sp
	204	1600	8	0.5	ol + gt

[a] = final run condition approached from 1525 °C

[b] = garnet composition reversed

[c] = duration in minutes for MEZO and HSS-15, all others in hours

ol, olivine; *opx*, orthopyroxene; *cpx*, clinopyroxene; *sp*, spinel; *gt*, garnet, *l*, liquid; *cm*, magnesite solid solution

Experiments on V25 and ^{57}Fe-Py employed Pt-Pt$_{90}$Rh$_{10}$ thermocouples, all other experiments employed Re$_3$-W$_{75}$ thermocouples; h, undetermined hydrous phase

and low (Run 273) temperature, and from two different peridotite starting compositions (KAP1 and a more Ca-rich, Mg-poor oceanic peridotite composition AB1, Table 1) suggest equilibrium garnet compositions were probably achieved in these experiments.

Thirdly, in one experiment at 5.5 GPa and 1450 °C (Run 386, Table 2), garnets seeds of different composition (natural Dora Maira pyrope Py$_{98}$Gr$_2$ and synthetic Py$_{25}$Gr$_{75}$) were loaded with the starting materials. The garnet rims grown on the seeds have compositions identical to those synthesized at the same conditions from the initial starting materials without garnet seeds (Fig. 2), indicating that garnets *synthesized* in all experiments probably represent equilibrium compositions. In this way, the garnet rims approached the equilibrium garnet composition from high Ca (Py$_{25}$Gr$_{75}$) or low Ca (Dora Maira-Py$_{98}$Gr$_2$) directions, and in all cases must take in Cr and Fe.

Reversals of garnet composition along the liquidus of the two komatiites were not attempted. Other studies have demonstrated that mineral compositions along the liquidi of ultramafic compositions at these extremely high temperatures (> 1800 °C) almost certainly represent equilibrium even with typical run durations of only 5 to 10 min (Herzberg et al. 1990).

Reversal of the spinel-garnet transition in spinel harzburgite SHZ1 was attempted at 5.5 GPa and 1450 °C (Run 386, Table 2). Seeds of garnet were loaded in with the SHZ1 starting material and run in the spinel stability field determined for this composition by synthesis experiments (line in Fig. 2). The reversals were unsuccessful, as garnet did not dissolve but grew in the latter experiment. Therefore, the spinel-garnet transition for this composition in Fig. 3 is suspect.

Results

Partitioning of Cr between garnet and ultramafic liquid

Partition coefficients were derived for Cr between liquid and garnet on the liquidus of both aluminium undepleted

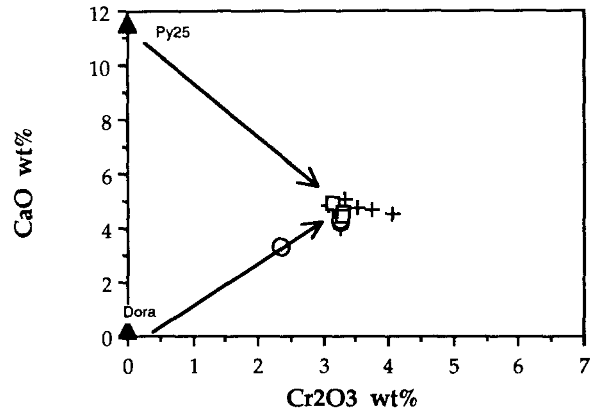

Fig. 2. CaO vs Cr_2O_3 plot for garnets from a reversal experiment at 5.5 GPa and 1450 °C. Note that garnets synthesized from peridotite KAP1 (*crosses*) overlap those grown as rims on seeds of Dora Maira pyrope (*open circles*) and synthetic $Py_{25}Gr_{75}$ garnet (*open squares*). Equilibrium was achieved from both high and low Ca directions (*arrows*). The original seed compositions are shown as *filled triangles*. + synthesis Gt, ○ Gt rim-Dora, □ Gt rim Py_{25}, ▲ seeds

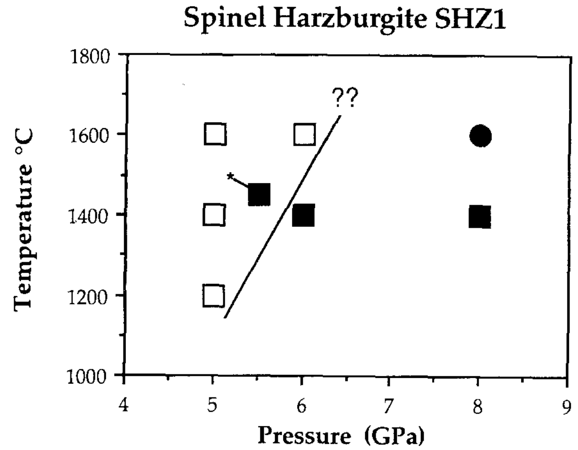

Fig. 3. Phase relationships for spinel harzburgite SHZ1. The *line with question marks* represents the spinel-garnet phase transition in this composition based on synthesis experiments. The *point labelled with an asterisk* represents a failed attempt to dissolve garnet seeds within the spinel stability field (as determined by the synthesis boundary). The synthesis boundary is therefore suspect. □ Ol–Opx–Sp, ■ Ol–Opx–Gt–Sp, ● Ol–Gt

komatiite and aluminium depleted komatiite (Wei et al. 1990), and above the solidus of peridotite KLB-1 (Takahashi 1986). Liquid analyses for these experiments are presented elsewhere (Trønnes et al. submitted), or are available from the first author upon request. The MgO contents of liquids in equilibrium with garnets in both studies are greater than 19 wt%, and these liquids are referred to here rather broadly as 'ultramafic'. Values for $D_{Cr}^{(gt/liq)}$ range from about 2 to 7 (Fig. 4) and there is some suggestion that $D_{Cr}^{(gt/liq)}$ decreases with increasing pressure, although the effects of bulk composition, temperature and oxidation state of Cr on $D_{Cr}^{(gt/liq)}$ are unknown given the current available data set.

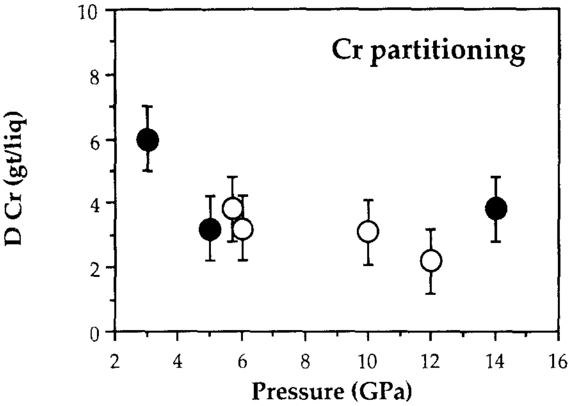

Fig. 4. Plot showing the effect of pressure on the partition coefficient ($D_{Cr}^{gt/liq}$) for Cr between garnet and ultramafic liquid. *Open symbols*, data from this study on aluminium undepleted komatiite and aluminium depleted komatiite. *Solid symbols*, derived from data given in Takahashi (1986)

Compositional variation in garnets

The 'lherzolite' boundary on a CaO vs Cr_2O_3 plot defining Ca saturation or undersaturation for garnets produced in experiments from this study is based on garnets from Kaapvaal xenoliths (Boyd and Nixon 1989), and is similar to one originally proposed by Sobolev et al. (1973) for Yakutian xenoliths.

Garnets along the liquidus of aluminium undepleted komatiite at 5.7 GPa, 6 GPa and 10 GPa, and along the liquidus of aluminium depleted komatiite at 12 GPa, all plot slightly below the lherzolite boundary on a Ca-Cr plot (Fig. 1) and have less than 3 wt% Cr_2O_3. Garnets coexisting with ultramafic melt above the solidus of fertile peridotite KLB1 at 5 and 14 GPa (Takahashi 1986) are slightly subcalcic, but those within the melting interval at 3 GPa are clearly Ca saturated. Garnets along both the peridotite solidus and komatiite liquidus contain less than 3 wt% Cr_2O_3 (Table 3) and thus although they are subcalcic, are depleted in Cr_2O_3 relative to the majority of garnets in diamonds or in garnet harzburgite xenoliths (Fig. 1).

Garnets coexisting with only olivine and orthopyroxene in the subsolidus of 'cratonic' peridotite KAP1 at 5 GPa and 1450 °C, or at higher pressures and temperatures (6 and 8 GPa, 1600 °C, Table 3) are also slightly Ca undersaturated (dark symbols, Fig. 1) but, in contrast to the komatiite liquidus garnets, they contain up to 4 wt% Cr_2O_3 (Table 3) and approach the Cr abundance of some mantle-derived low Ca garnets. Garnets crystallized from KAP1 at lower temperatures plot in the field of Ca saturation (Fig. 1).

Garnets crystallized within the melting interval of V25 (and V25 + Cr) from the assemblage garnet harzburgite + liquid at 1075 °C and 6 GPa are also subcalcic (Fig. 1). Garnets not shown in Fig. 1, but which crystallized at lower temperatures within the melting interval of V25 at 6 GPa coexist with clinopyroxene (Table 2) and are Ca saturated (Table 3).

Low Ca garnet, olivine and orthopyroxene coexist with Cr-rich spinel in SHZ1 between about 6 and 8 GPa

Table 3. Garnet analyses

Run	217	216	263	273	276	286	292	305	306		
Sample	KAP1	KAP1	KAP1	KAP1	KAP1	KAP1	KAP1	KAP1	KAP1		
MgO	22.98	25.31	22.87	21.71	22.01	22.09	20.91	22.10	21.92		
Al_2O_3	20.31	21.21	20.40	20.75	18.72	19.71	21.00	20.11	20.01		
SiO_2	42.72	43.00	42.63	42.62	42.21	42.91	43.02	43.41	43.21		
CaO	4.30	4.21	4.00	5.54	5.21	5.42	6.33	5.31	5.92		
Cr_2O_3	3.71	1.62	3.93	3.74	3.81	3.72	3.53	4.14	3.91		
FeO	6.21	6.53	6.25	6.22	6.84	6.81	6.10	6.31	5.82		
Total	100.23	101.88	100.08	100.58	98.80	100.66	100.89	101.38	100.80		
Mg#	0.87	0.87	0.87	0.86	0.85	0.85	0.85	0.86	0.87		
Cr#	0.11	0.05	0.11	0.11	0.12	0.11	0.10	0.12	0.12		
Wo	0.108	0.105	0.101	0.152	0.132	0.135	0.157	0.131	0.146		
En	0.802	0.877	0.800	0.690	0.777	0.764	0.724	0.759	0.756		
Fs	0.090	0.018	0.099	0.159	0.091	0.101	0.119	0.110	0.098		
CA	0.082	0.080	0.016	0.105	0.102	0.104	0.119	0.100	0.112		
CRAL	0.239	0.234	0.242	0.243	0.229	0.239	0.242	0.237	0.236		
MGFE	0.679	0.686	0.682	0.651	0.669	0.669	0.638	0.663	0.652		
Temp	1600	1600	1450	1300	1450	1450	1300	1300	1400		
P(GPa)	6	8	5	5	7	6	5	5	5		
Run	242	569	168	247	128	184	223	381	204	180	156
Sample	HSS15	M620	M620	M620	V25	V25	V25	V25 + Cr	SHZ1	SHZ1	SHZ1
MgO	24.81	25.12	25.15	23.50	26.25	27.48	25.98	25.05	23.41	23.57	22.73
Al_2O_3	20.20	20.91	21.70	21.82	24.57	24.74	24.75	15.26	3.61	4.91	14.65
SiO_2	45.20	44.10	44.12	43.54	43.75	43.55	44.86	41.92	39.21	41.41	41.93
CaO	4.00	3.51	3.51	3.72	4.88	3.76	5.04	4.52	0.80	0.62	2.65
Cr_2O_3	0.71	1.13	1.12	1.20	0.00	0.00	0.00	11.99	25.71	22.86	10.40
FeO	4.91	4.93	5.15	5.42	0.00	0.00	0.00	0.00	6.30	6.11	6.85
Total	99.83	99.70	100.77	99.20	99.45	99.53	100.6	98.78	99.00	99.48	99.21
Mg#	0.90	0.90	0.90	0.89	0	0	0	0	0.87	0.87	0.85
Cr#	0.02	0.03	0.03	0.04	0	0	0	0.35	0.83	0.75	0.32
Wo	0.087	0.085	0.085	0.091	0.118	0.067	0.122	0.115	0.020	0.016	0.068
En	0.836	0.848	0.848	0.805	0.882	0.910	0.878	0.885	0.890	0.859	0.807
Fs	0.076	0.067	0.067	0.104	0	0	0	0	0.090	0.125	0.125
CA	0.075	0.066	0.066	0.070	0.089	0.068	0.092	0.087	0.017	0.013	0.052
CRAL	0.212	0.225	0.231	0.234	0.246	0.245	0.248	0.246	0.239	0.226	0.233
MGFE	0.713	0.709	0.704	0.696	0.665	0.688	0.660	0.668	0.745	0.762	0.715
Temp	1900	1800	1800	1860	1000	1075	925	1075	1600	1400	1400
P(GPa)	12	5.7	6	10	6	6	6	6	8	8	6

All Fe as FeO. Mg# = Mg/(Mg + Fe) Cr# = Cr/(Cr + Al) CA = Ca/(Ca + (Cr + Al) + (Mg + Fe)) CRAL = (Cr + Al)/(Ca + (Cr + Al) + (Mg + Fe)), MGFE = (Mg + Fe)/(Ca + (Cr + Al) + (Mg + Fe)) on atomic basis.

Temperatures in °C. Analyses represent the average of 4 to 6 garnet analyses in each run product.

The ferric iron content of garnet in all experiments above is estimated to be less than 9% of total Fe (Table 4), based on the ^{57}Fe Mössbauer spectrum of a ^{57}Fe-enriched pyrope synthesized in a graphite capsule at 7 GPa and 1300 °C (*Table* 2). Similar amounts of ferric iron are present in natural low Ca garnets (Luth et al. 1990)

Table 4. ^{57}Fe Mössbauer parameters of synthetic garnet[a]

Sample	Fe^{2+}			Fe^{3+}			$Fe^{3+}/\Sigma Fe$	X^2
	IS	QS	FWHH	IS	QS	FWHH		
^{57}Fe-Py	1.28	3.61	0.28	0.19	0.42	0.48	0.09	279

Measurements performed at 298K on pyrope containing 2 wt% ^{57}Fe-enriched Fe_2O_3.

Synthesis conditions are given in Table 2. Sample preparation and data collection for Mössbauer spectroscopy as in Canil and Muehlenbachs (1990). Spectra were fit with one symmetric doublet for Fe^{2+}, and one symmetric doublet for Fe^{3+}

[a] All parameters given relative to Fe metal at 298 K

IS = isomer shift, QS = quadropole splitting, FWHH = Full width at half maximum

depending on temperature (Table 2). At pressures below about 5 GPa at 1200 °C, 6 GPa at 1400 °C, or 7 GPa at 1600 °C, a garnet-free spinel harzburgite assemblage is stable (Fig. 3). The spinel-garnet transition for this composition is shifted to such high pressures because of its extremely high Cr/Cr + Al, compared to more typical mantle peridotites and harzburgites, which generally have Cr/Cr + Al less than about 0.15 and 0.25, respectively, and form garnet lherzolite assemblages at pressures of 2.5 to 3.0 GPa. At pressures at or about 8 GPa, orthopyroxene and spinel in SHZ1 are eventually consumed according to the reaction:

$$\begin{array}{ccccccc} 2\,Mg_2Si_2O_6 & + & MgAl_2O_4 & = & Mg_3Al_2Si_3O_{12} & + & Mg_2SiO_4 \\ \mathrm{Opx} & & \mathrm{Sp} & & \mathrm{Gt} & & \mathrm{Ol} \end{array} \quad (1)$$

In a multi-component composition such as SHZ1, this reaction is not univariant, and occurs over a broad pressure interval (Fig. 3, see also O'Neill 1981; Chatterjee and Terhart 1985).

Garnets crystallized from spinel harzburgite SHZ1 are clearly the most subcalcic and Cr-rich of all the experimentally produced garnets presented in this study (Table 3, Fig. 1). Garnets crystallized at 6 GPa and 1400 °C overlap with compositions for the more Cr-rich, low Ca garnets included in diamonds. Garnets crystallized from SHZ1 at 8 GPa at either 1400 or 1600 °C are similar to the most Cr-rich, low Ca garnets observed in nature (21 wt% Cr_2O_3-N.V. Sovolev, pers. comm. 1991).

Effects of temperature and pressure on garnet composition

For a given bulk composition, garnets contain higher Ca (or grossular components) with decreasing temperature at constant pressure, or with increasing pressure at constant temperature (Fig. 5). These observations are consistent with other experimental studies on Ca partitioning between garnet and pyroxenes (Yamada and Takahashi 1984; Brey et al. 1990). The effect of increased pressure at constant temperature does not appear to be significant at pressures above about 6 GPa.

The Cr concentrations in subsolidus lherzolitic and liquidus komatiitic garnets are not affected by pressure, in contrast to the garnets in spinel harzburgite SHZ1. In SHZ1 at constant temperature, Cr partitions more strongly into garnet with increased pressure. This observation is consistent with phase equilibria for garnets on the join pyrope-knorringite which show that with increasing pressure at constant temperature, garnets richer in knorringite component are stable along the join (Irifune et al. 1982; Irifune and Hiraya 1983). Similar observations were noted by Brey et al. (1991).

The strong effect of temperature on garnet composition (Fig. 5) must be considered before direct application of garnet compositions from this study to natural examples discussed below. For example, many low Ca garnets sampled in the mantle equilibrated at significantly lower temperatures (< 1200 °C) than the garnets produced in this study (> 1300 °C). By analogy with Al, it is conceivable that Cr is preferentially partitioned into garnet relative to coexisting orthopyroxene with decreasing temperature and increasing pressure. For instance, the knorringite component of garnets stable along the join pyrope-knorringite increases with decreasing temperature at constant pressure (Irifune and Hariya 1983). This trend is not, however, observed experimentally in Ca-bearing systems. For a given bulk composition, garnets rapidly become calcic with decreased temperature at constant pressure, with essentially no simultaneous change in Cr content (Fig. 5, see also Brey and Köhler 1990).

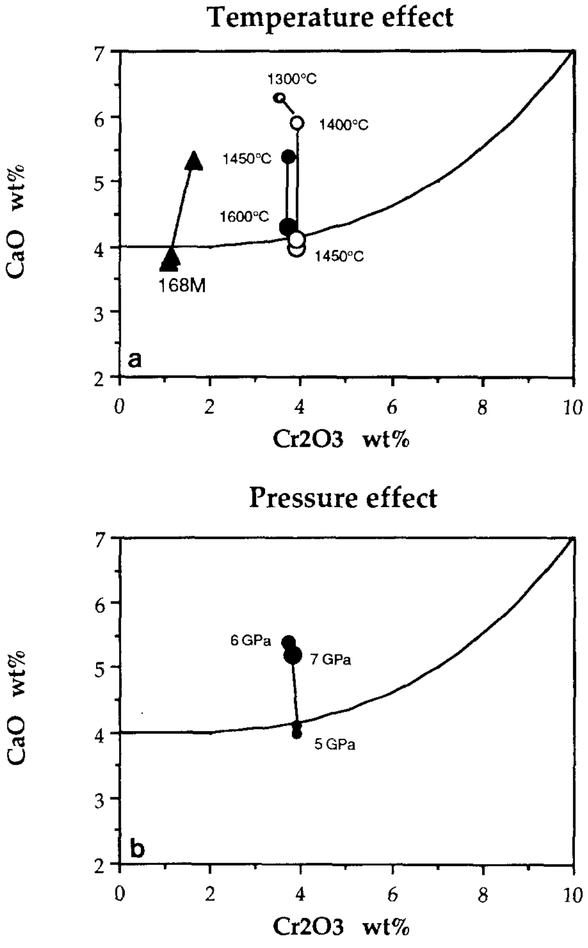

Fig. 5. a CaO vs Cr_2O_3 plot showing effect of temperature on garnet compositions from bulk compositions KAP1 and aluminium undepleted komatiite M620 (*triangles*). The size of the symbol represents the decrease in temperature, at constant pressure (5 GPa). The *solid triangles* labelled 168M represent garnet analyses along the thermal gradient in a liquidus experiment (168M) on aluminium undepleted komatiite M620 (Table 2). Garnets within the hot spot of this experimental charge are sub-calcic but shift drastically into the Ca-saturated field due to only a slight change in temperature along the thermal gradient (50 °C) in the charge. **b** CaO vs Cr_2O_3 plot showing effect of pressure at constant temperature (1450 °C) on garnet compositions crystallized from cratonic peridotite KAP1.

These observations highlight the strong effect of bulk composition on the Cr contents of experimentally produced garnets, also noted by Brey and Köhler (1990). This effect is borne out in recent data for rare low Ca garnet harzburgite xenoliths from southern Africa which show that xenoliths containing the highest bulk Cr/Cr + Al, have garnets with low modal abundance but high Cr_2O_3 (Boyd et al. submitted).

Discussion

Constraints on available hypotheses

Garnets in equilibrium with ultramafic liquid along the liquidus of komatiites, within the melting interval of peridotite, and in the subsolidus of cratonic peridotites thought to be residues of ultramafic liquid removal (e.g. Boyd 1989), contain significantly less Cr_2O_3 than the majority of natural low Ca garnets (Fig. 1). Partition coefficients for Cr between garnet and ultramafic liquid (Fig. 4) require multiple melt extractions to explain the high Cr_2O_3 contents of natural low Ca garnets. For example, a peridotite that contained 2000 to 4000 ppm Cr would have residual garnets upon melting that contained only 2 to 4 wt% Cr_2O_3, assuming a $D_{Cr}^{(gt/liq)}$ of seven, the highest observed in this study (Fig. 4). At least one additional melting event would be required to elevate Cr_2O_3 contents of residual garnets to greater than 4 wt% Cr_2O_3. For garnet to remain within the melting interval of peridotite during repeated melt extraction, multi-stage melting events must have occurred at pressures above 5 GPa. At lower pressures, the stability field of garnet above the peridotite solidus is reduced (Takahashi 1990), and this phase should be consumed by melting before its Cr_2O_3 content approached that of natural low Ca garnets.

Garnets crystallized from a garnet harzburgite + liquid assemblage in the system CMAS–CO_2–H_2O with or without Cr_2O_3 at 1075 °C and 6 GPa are subcalcic (Fig. 1). If it is assumed that this pressure, temperature and assemblage depicts that of a depleted harzburgite, serpentinized and metamorphosed to similar P-T conditions (Schulze 1986), then the hypothesis that low Ca garnets in the upper mantle crystallized from serpentinite subducted to high pressures seems quite viable.

Unlike all other compositions investigated, the extremely depleted and Cr-rich spinel harzburgite SHZ1 crystallized extremely Ca-poor, Cr-rich garnets, at P-T conditions similar to those deduced for diamonds and xenoliths containing low Ca garnets (5 to 7 GPa, Boyd et al. 1985; Kesson and Ringwood 1989). These observations are consistent with the proposal that low Ca garnets crystallized from multiply depleted harzburgite subducted and accreted to the mantle roots of cratons (Ringwood 1977; Kesson and Ringwood 1989).

Low Ca garnets – a dual origin?

A single model for the origin of low Ca garnets in diamond has been difficult to obtain due to the numerous exceptions inherent in the paragenesis of low Ca garnets (Boyd and Nixon, submitted). Models proposed by various workers thus far can account quite elegantly for a given particular feature of low Ca garnets (e.g. low Ca, high Cr content), but may fail to explain other characteristics (e.g. coexisting mineral assemblages, trace element geochemistry). Two models for the origin of low Ca garnets, based on previous hypotheses, but taking into account the experimental constraints presented in this study, are developed below.

It is clear from the present results that garnets remaining after ultramafic liquid removal would not be sufficiently subcalcic or Cr-rich unless subjected to multiple events of melting. If such multi-stage melting is feasible, and indeed formed harzburgites within Archean cratonic lithospheres (e.g. Nixon et al. 1987), then the Boyd and Gurney (1982) hypothesis would explain the origin of low Ca garnets in harzburgite xenoliths with cratonic compositional affinity. The chemistry of such xenoliths is quite distinct from that of abyssal peridotites and harzburgites (Boyd et al. submitted), and thus they cannot represent subducted mid-ocean ridge harzburgite or abyssal serpentinite metamorphosed in the garnet facies, as would be advocated by the Schulze (1986) and Kesson and Ringwood (1989) hypotheses.

Although the occurrence of low Ca garnets in harzburgite xenoliths with cratonic compositional affinity is best explained by the Boyd and Gurney (1982) hypothesis, those in diamonds are more in accord with hypotheses of Schulze (1986) and Kesson and Ringwood (1989). Orthopyroxene is very abundant in low Ca garnet harzburgite xenoliths, yet there is a general paucity of this phase in diamonds containing low Ca garnets (Meyer 1987; Kesson and Ringwood 1989). Moreover, olivines, orthopyroxenes and spinels coexisting with low Ca garnets included in diamonds are more Cr- and Mg-rich, compared with those in garnet harzburgite xenoliths (Hervig et al. 1980; Kesson and Ringwood 1989) although some overlap is evident (Boyd et al. submitted). These factors, coupled with the experimental evidence described above, argue for a protolith for low Ca garnets in diamonds which is generally more Mg- and Cr-rich than typical low Ca garnet harzburgite, and which contains less modal orthopyroxene. Very depleted harzburgite, or its hydrated equivalent (serpentinite), would be a suitable protolith from which low Ca garnets in diamonds could have crystallized. Experiments presented herein on spinel harzburgite with Cr/Cr + Al of 0.84 suggest that such a protolith is required to crystallize low Ca garnets in diamonds with high Cr_2O_3 and little if any CaO. Possible natural analogues of such a depleted protolith are harzburgites from ophiolites in the Papuan Ultramafic Belt, which have Cr/Cr + Al of up to 0.8 (Jaques and Chappell 1980). The high Cr/Cr + Al of such bulk compositions explains not only the Cr-rich nature of many garnets and olivines in diamonds (Hervig et al. 1980; Meyer 1987), but also the presence of chromite-rich spinel in diamonds, which could only have crystallized within the diamond stability field as a result of the effect of Cr/Cr + Al in increasing the stability field of spinel lherzolite (Fig. 6).

Rare earth element (REE) patterns for low Ca garnets extracted from heavy mineral concentrate, xenoliths or diamonds in all but one case show LREE enrichment (Richardson et al. 1984; Shimizu and Richardson 1987; Nixon et al. 1987) which is inconsistent with a simple one stage origin for these garnets as residues of melt extraction in either the MORB or komatiite source region. The REE patterns are indicative of metasomatic processes recorded by low Ca garnets after their original formation, but in some cases, preceeding the formation of diamonds. The metasomatism may be linked with carbonation of the host rock for diamonds by kimberlitic melts (Richardson et al. 1984) but consideration of available partition coefficients for REE in garnets argues against this simple relationship (Shimizu and Richardson 1987). Some low Ca garnets can contain up to 40 ppm Sr (J. Gurney, pers. comm.) arguing for the former coexistence of carbonate with such garnets (e.g. Boyd and Gurney 1982). Experimentally derived partition coefficients for Ca, Sr, Cr and the REE between

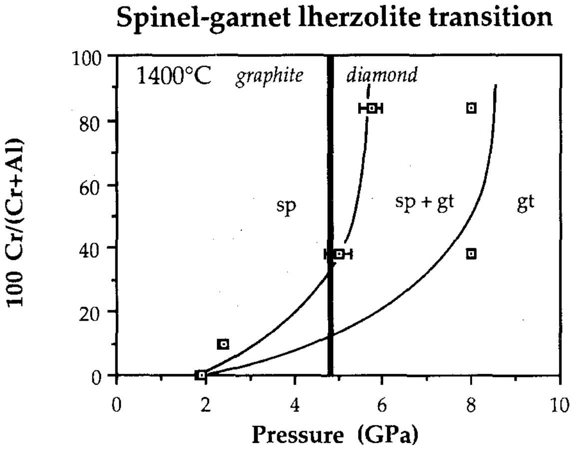

Fig. 6. Estimated effect of Cr/Cr + Al on the spinel to garnet lherzolite transition at 1400 °C. Note the high bulk Cr/Cr + Al required of any diamond protolith to crystallize both spinel and garnet as inclusions in diamond. Data points for bulk compositions with 100 Cr/Cr + Al = 84 are from this study (spinel harzburgite composition SHZ1) and those for bulk compositions with 100 Cr/Cr + Al = 38 and 11 are from Irifune and Ringwood (1987) and Green and Ringwood (1967), respectively. Data at Cr/Cr + Al = 0 are for the CaO–MgO–Al_2O_3–SiO_2 system (O'Hara et al. 1971) adjusted for the effect of 10 mol%Fe_2SiO_4 component in olivine on the transition (after O'Neill 1981). The graphite-diamond transition (G–D) at 1400 °C is after Kennedy and Kennedy (1976)

garnet and carbonate would be most useful in future attempts to explain the trace element distributions in low Ca garnets, and their bearing on the origin of diamonds.

Conclusions

The major conclusions drawn from interpretations of experimental data presented in this study are as follows:

1. The more Cr-poor (< 4 wt% Cr_2O_3) population of low Ca garnets occurring as xenocrysts dispersed in kimberlite, as inclusions in diamond, or as constituent minerals in rare garnet harzburgite xenoliths from southern Africa, could have originated as residues of *one stage* of ultramafic melt removal during melting events at high pressures (> 3 GPa) in the Archean mantle (e.g. Boyd and Gurney 1982). The more Cr-rich (> 3 wt% Cr_2O_3) population of low Ca garnets requires multiple melt extraction if they originated by such a process.
2. Low Ca garnets with greater than 4 wt% Cr_2O_3 that coexist with spinel as inclusions in diamonds probably crystallized from very depleted, Cr-rich (Cr/Cr + Al > 0.3) harzburgite or dunite protoliths. This explains both the high Cr content of such garnets, and their occurrence with spinel in the diamond stability field (Fig. 6). Candidate protoliths would be similar to Cr-rich harzburgites found in some ophiolite complexes, thought to represent the residue of melt extraction at shallow levels (< 1 to 2 GPa) in the mantle. The protoliths for low Ca garnets in Precambrian diamonds coexisting with spinel, probably originated by multi-stage melt removal, perhaps within a Precambrian mid-ocean ridge environment, where such harzburgites could have formed. Whether such protoliths for low Ca garnets were dry or wet (serpentinized) prior to subduction and metamorphism within the diamond stability field is not resolvable. For this reason, the hypotheses of Schulze (1986) and Ringwood (1977) for the origin of low Ca garnets are essentially equivocal in terms of explaining the low Ca nature of such garnets. Oxygen isotope studies of low Ca garnets hosted in diamonds or in xenoliths would be helpful in distinguishing whether the protolith for low Ca garnets was serpentinized prior to subduction and metamorphism to the garnet facies.

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