Geology

An exsolution origin for Archaean mantle garnet

--Manuscript Draft--

Manuscript Number:	G39680R1
Full Title:	An exsolution origin for Archaean mantle garnet
Short Title:	An exsolution origin for Archaean mantle garnet
Article Type:	Article
Keywords:	Garnet, craton, mantle, peridotite, exsolution, orthopyroxene
Corresponding Author:	Emma Tomlinson Trinity College Dublin School of Natural Sciences Dublin, Dublin IRELAND
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Trinity College Dublin School of Natural Sciences
Corresponding Author's Secondary Institution:	
First Author:	Emma L Tomlinson
First Author Secondary Information:	
Order of Authors:	Emma L Tomlinson
	Balz S Kamber
	Brendan C Hoare
	Stead V Stead
	Benoit Ildefonse
Order of Authors Secondary Information:	
Manuscript Region of Origin:	SOUTH AFRICA
Abstract:	<p>It is well established that the cratonic sub-continental lithospheric mantle (C-SCLM) represents a residue of extensively melted peridotite. The widespread occurrence of garnet in C-SCLM remains a paradox because experiments show that it should be exhausted beyond c. 20% melting. It has been suggested that garnet may have formed by exsolution from Al-rich orthopyroxene, however, the few documented examples of garnet exsolution in cratonic samples are exotic and do not afford a direct link to garnet in granular harzburgite.</p> <p>We report crystallographic, petrographic and chemical data for an exceptionally well-preserved orthopyroxene megacryst containing garnet lamellae, juxtaposed against granular harzburgite. Garnet lamellae are homogenously distributed within the host orthopyroxene and occur at an orientation that is unrelated to orthopyroxene cleavage, strongly indicating that they formed by exsolution. Garnet lamellae are sub-calcic Cr-pyrope and the orthopyroxene host is high-Mg enstatite, these phases equilibrated at 4.4GPa, 975oC. The reconstructed precursor is a high-Al enstatite that formed at higher pressure and temperature conditions of c. 6GPa and 1750oC.</p> <p>The megacryst shows evidence for disintegrating into granular peridotite, and garnet and orthopyroxene within the granular peridotite are texturally and chemically identical to equivalent phases in the megacryst. Collectively, this evidence supports a common origin for the granular and exsolved portions of the sample. We hypothesize that high-Al enstatite was a common phase in the C-SCLM and that exsolution during cooling and stabilization of the C-SCLM could be the origin of most sub-calcic garnets in depleted peridotites.</p>

An exsolution origin for Archaean mantle garnet

Emma L. Tomlinson¹, Balz S. Kamber¹, Brendan C. Hoare¹, Clare V. Stead¹,
Benoit Ildefonse²

¹Department of Geology, Trinity College Dublin, Dublin 2, Ireland

²Géosciences Montpellier, CNRS, Université Montpellier, Montpellier, France.

ABSTRACT

It is well established that the cratonic sub-continental lithospheric mantle (C-SCLM) represents a residue of extensively melted peridotite. The widespread occurrence of garnet in C-SCLM remains a paradox because experiments show that it should be exhausted beyond *c.* 20% melting. It has been suggested that garnet may have formed by exsolution from Al-rich orthopyroxene, however, the few documented examples of garnet exsolution in cratonic samples are exotic and do not afford a direct link to garnet in granular harzburgite.

We report crystallographic, petrographic and chemical data for an exceptionally well-preserved orthopyroxene megacryst containing garnet lamellae, juxtaposed against granular harzburgite. Garnet lamellae are homogenously distributed within the host orthopyroxene and occur at an orientation that is unrelated to orthopyroxene cleavage, strongly indicating that they formed by exsolution. Garnet lamellae are sub-calcic Cr-pyroxene and the orthopyroxene host is high-Mg enstatite, these phases equilibrated at 4.4GPa, 975°C. The reconstructed precursor is a high-Al enstatite that formed at higher pressure and temperature conditions of *c.* 6GPa and 1750°C.

The megacryst shows evidence for disintegrating into granular peridotite, and garnet and orthopyroxene within the granular peridotite are texturally and chemically identical to equivalent phases in the megacryst. Collectively, this evidence supports a common origin for the granular and exsolved portions of the sample. We hypothesize that high-Al enstatite was a common phase in the C-SCLM and that exsolution during cooling and stabilization of the C-SCLM could be the origin of most sub-calcic garnets in depleted peridotites.

INTRODUCTION

The Earth's ancient cratonic sub-continental lithospheric mantle (C-SCLM), which makes up the roots of continental shields, is distinctly different in composition to oceanic and off-craton mantle. C-SCLM is characterized by uniformly high Mg# (>92) and extreme depletion in FeO, CaO, Al₂O₃ and Na₂O and is widely considered to be the residue of very high degree melting (up to 40%) of the convecting mantle (Boyd, 1989, Boyd and Mertzman, 1987). The conditions under which such melting took place continue to be debated, with models ranging from low pressure settings at ocean ridges (Canil, 2004) or arcs (Kelemen et al., 1998, Parman et al., 2004, Simon et al., 2007), or at high pressure in a very hot plume (Herzberg, 1993, Griffin et al., 2003, Arndt et al., 2009). The C-SCLM has remained tectonically stable and isolated from mantle convection since its formation between 3.5 and 2.5 Ga (Pearson et al., 1995).

Depleted cratonic peridotites typically contain 5-10% chrome pyrope garnet. This abundance of garnet is difficult to reconcile with experimental studies on fertile peridotite, which indicate that garnet should be exhausted by <<20 % melting of pyrolite mantle (Walter, 1998, Herzberg, 2004). One model to explain this paradox

proposes that sub-calcic garnets formed metasomatically due to percolation of reduced, asthenosphere-derived fluids (Malkovets et al., 2007) and/or carbonatite-kimberlite melts (Bell et al., 2005). Alternatively, Cox et al. (1987) suggested that most garnet in Archean SCLM peridotites was formed by exsolution from an Al-rich pyroxene precursor in the depleted residue. Their model is supported by the spatial relationship between garnet and orthopyroxene (Saltzer et al., 2001) and by experimental phase equilibria (Canil, 1991, Canil, 1992). Examples of garnet exsolution in Cr-rich orthopyroxene megacrysts have been described from several cratons (Aoki et al., 1980, Dawson et al., 1980, Dawson, 2004, Gibson, 2017, Wasch et al., 2009). However, thus far no direct link between these rare exsolved garnet and the distinct grains that occur in granular harzburgite has been convincingly demonstrated.

Here, we present crystallographic, textural and chemical data for a well-preserved orthopyroxene-garnet megacryst encased in a granular Kaapvaal Craton peridotite composed of equivalent phases and olivine and discuss the evidence for exsolution of garnet in the C-SCLM.

SAMPLE AND METHODS

The Kaapvaal SCLM extends to a depth of ~200km, from which xenoliths have been brought to the surface by numerous kimberlites. Sample BP002, from the Bultfontein pans (-28.739155, 24.818094), is a garnet harzburgite xenolith dominated by a large (15x12x7cm) orthopyroxene megacryst containing garnet lamellae, juxtaposed against coarse granular harzburgite (Fig. 1a). [Field counting estimates suggest that such samples make up 0.5-1% of the xenolith cargo at this locality \(this study, Wasch et al. 2009\).](#) Garnet and orthopyroxene in both the megacryst and host xenolith were

analyzed for their major and trace element compositions by SEM-EDS and LA-ICP-MS at Trinity College Dublin. Orientations of orthopyroxene and garnet within the megacryst were determined by EBSD at Geosciences Montpellier. Further details are provided in the Data Repository. All errors are 2σ .

RESULTS

Petrology

The megacryst contains 10.4% garnet lamellae, while the granular harzburgite portion of the xenolith comprises 53% olivine, 40% orthopyroxene and 7% garnet. Garnet occurs sporadically throughout the harzburgite as subhedral equant grains most often spatially associated with coarse (typically 2-3mm) orthopyroxene grains. These commonly display strain birefringence, while olivine and garnet are less strained (Fig. 1b). The boundary between the orthopyroxene megacryst and the host granular xenolith is transitional over ~2cm (Fig. 1a). Thus, the megacryst appears to have physically disintegrated into the coarse granular harzburgite. Orthopyroxene subgrains within the transitional zone are highly strained.

Crystallography

The garnet lamellae occur at regularly spaced intervals (~4mm) and have a homogeneous distribution within the host orthopyroxene. The EBSD data show that there are two populations of lamellae, the first set oriented parallel to {001} of the orthopyroxene host, the second set cross-cutting the first at 30°, forming a conjugate set parallel to {011} and {0-11} of the orthopyroxene host (Fig. 2a,c). Importantly, this orientation shows that the garnet lamellae do not occur along the cleavage directions of the host. Garnet crystals have a strongly preferred crystallographic axis

alignment fabric, with separate grains, grains in different lamellae and grains from all lamellae populations being orientated at a systematic, acute angle to orthopyroxene (Fig. 2b,d).

Geochemistry

Garnet lamellae within the orthopyroxene megacryst are Cr-pyropes with Mg# 86.2 and plot in field of G9 calcic (Iherzolitic) garnet (Sobolev et al., 1973), the most common garnet type in Kimberley xenoliths (Dawson and Stephens, 1975). Garnet lamellae have sinusoidal chondrite normalized rare earth element (REE) patterns with a peak at Sm ($Sm_N = 16.1 \pm 1.8$) (Fig. 3a), typical of garnet from highly depleted Archaean peridotites. Significantly, garnets within the xenolith are identical to those in the exsolved sample, with all elemental concentrations agreeing within analytical error.

The megacryst is an enstatite with high Mg# (94.1) and moderate Al_2O_3 and CaO (0.74 ± 0.06 and 0.33 ± 0.04 wt%, respectively) and is typical of orthopyroxenes found in garnet-bearing mantle peridotite. Orthopyroxene shows slight Si depletion (0.24 wt% lower) and Al-enrichment (0.16 wt% higher) adjacent to garnet (S4). The REEs in the orthopyroxene also have a humped pattern with a peak at Sm ($Sm_N = 0.16 \pm 0.03$) (Fig. 3b), similar to patterns previously described for orthopyroxene in granular garnet peridotites (e.g. Simon et al., 2007). Orthopyroxenes within the xenolith are identical to those in the exsolved sample, with all elemental concentrations agreeing within analytical error.

The composition of the precursor phase, constructed using the modal proportions and compositions of the garnet and orthopyroxene in the megacryst, is $Wo_{1.4}En_{92.2}Fs_{6.4}$. This high-Al enstatite has Mg# 93.6 and high Al_2O_3 , CaO and low

SiO₂, relative to the exsolved orthopyroxene. There is good agreement between observed and predicted orthopyroxene/garnet trace element ratios (S4) indicating that the two phases are in equilibrium.

DISCUSSION

Evidence for exsolution

The mechanism of garnet formation by exsolution from orthopyroxene is supported by the homogenous and regular distribution of garnet lamellae within the megacryst and by the consistent orientation of garnet lamellae, which is unrelated to the orthopyroxene cleavage. In contrast, if the garnets were metasomatic, the orthopyroxene cleavage planes would control the orientations of garnet lamellae and regular distribution would be unexpected. Furthermore, the principal axis alignment of individual garnets both within and between lamellae suggests controlled garnet growth. An isochemical origin for garnet and enstatite is also supported the occurrence of compositional halos around garnet lamellae, which indicate that garnet nucleation and growth was driven by diffusion (closed system) rather than metasomatic (open system) processes (Chin et al., 2012, Chin et al., 2015).

Similar exsolved samples have previously been described from the SCLM (Aoki et al., 1980, Dawson, 2004, Dawson et al., 1980, Gibson, 2017), but what is significant about BP002 is the visible physical disintegration of the megacryst into the main body of the xenolith. Several observations suggest that garnet and orthopyroxene throughout the granular portion of sample BP002 likely originated from structural break-up of exsolved orthopyroxene-garnet megacrysts: the presence of strained orthopyroxene amongst the relatively unstrained olivine and garnet; the occurrence of garnet inclusions in orthopyroxene; and the identical compositions of

megacrystic and xenolithic phases. Exsolved megacryst disintegration could explain the spatial association of garnet and orthopyroxene more generally seen in granular peridotites (Cox et al., 1987, Saltzer et al., 2001).

On the basis of the observed modal abundance of orthopyroxene and garnet in the megacryst and granular peridotite, exsolution may account for 60% of garnet in the xenolith. In view of the similarity of garnet and enstatite between BP002 and typical Archaean granular peridotites, we hypothesize that high-Al enstatite was a common phase in C-SCLM and that exsolution is the likely origin of many sub-calcic garnets in depleted peridotites. Formation of garnet by exsolution from orthopyroxene is consistent with the low Al-Cr contents of Archaean peridotite xenoliths which indicate that little or no garnet was left in the original melt residue (Griffin et al., 2003).

Sinusoidal REEs

Sinusoidal REE patterns are widely attributed to the interaction of pre-existing grains with percolating LREE-rich fluids (Stachel et al., 1998) or carbonatitic melts (Shu and Brey, 2015). In the case of BP002, the attainment of trace element equilibrium between the two phases and Al-enrichment halos indicate that the sinusoidal REE patterns predate garnet exsolution. Accordingly, the observed REE patterns may have resulted from a metasomatic event that occurred prior to garnet exsolution or they may reflect the petrogenesis of the precursor orthopyroxene.

Formation of the precursor phase

Geothermobarometry of the exsolved megacryst and granular peridotite yield indistinguishable pressures and temperatures of 4.4 ± 0.9 GPa (Al in orthopyroxene

barometer (Brey et al., 1990)) and $975\pm 17^\circ\text{C}$ (Fe-Mg exchange thermometer, Harley (1984)). Of greater petrologic interest is the formation regime of the precursor orthopyroxene that must have originated above the peridotite solidus as a residue of partial melting. Tschermak substitution ($\text{Si}_4 + \text{M}^{+2} \rightarrow 2\text{Al}_3$) forms Al-rich orthopyroxene at high temperatures between pressures of 3 to at least 7GPa (Canil, 1991, Canil, 1992, Walter, 1998). Thermodynamic modeling in the model system CaO-MgO- Al_2O_3 - SiO_2 (CMAS, (Gasparik, 2000)) indicates that the precursor pyroxene with the observed Tschermak content intersects the solidus at 5.9GPa and 1750°C (Fig. 4). Constraints from experiments on natural compositions place the precursor formation depth at 5.0-6.3GPa (Canil, 1991, Canil, 1992, Walter, 1998). The observed Tschermak composition also intersects the solidus in the model CMAS system within the plagioclase stability field at 0.3GPa and 1260°C (Fig. 4). Therefore, the more likely inferred origin is very high P and T.

Collectively, these findings argue against root formation of the Kaapvaal craton by stacking of shallow residual lithosphere in a collisional setting (Kelemen et al., 1998, Parman et al., 2004, Simon et al., 2007). Instead, the observations and data are consistent with the C-SCLM representing the refractory residue after high-degree melting at depth, for example in a hot plume (Herzberg, 1993, Griffin et al., 2003, Arndt et al., 2009) yielding an extracted melt of broadly komatiitic composition. High-degree melting in a hot plume is capable of producing the high-Mg# (low-density), anhydrous (high viscosity) conditions necessary for the long-term stability of the Archaean lithospheric mantle.

CONCLUSIONS

200 This study documents an unequivocal link between an exceptionally well-
201 preserved exsolved garnet-orthopyroxene megacryst and sub-calcic garnet in
202 Archaean granular peridotites. The exsolved megacryst shows evidence for
203 disintegrating into granular peridotite. Furthermore, equivalent phases within the
204 megacryst and granular portions of the xenolith are chemically and texturally
205 identical. The compositions of the exsolved garnets and orthopyroxene are typical of
206 those from harzburgites and depleted lherzolites from the SCLM, therefore we
207 suggest that exsolution from high-Al enstatite could be the origin of most sub-calcic
208 garnets in depleted peridotites.

209 The reconstructed precursor phase was a high-Al enstatite, which formed at
210 higher temperature and somewhat greater depth (ca. 6GPa, 1750°C) than the
211 equilibration conditions of the exsolved phases (4.4GPa, 975°C), likely as a residue
212 after deep, high-degree melting. Strongly sub-calcic garnet is unique to Archaean
213 SCLM, therefore its formation by isochemical exsolution is intimately related to the
214 formation mechanism and cooling history of the Archaean SCLM.

215

216 **Acknowledgements** This manuscript benefited from constructive reviews from Dante
217 Canil, Emily Chin and one anonymous reviewer. We would like to thank the
218 following for help and advice: Jock Robey (sampling), Paul Guyett (SEM-EDS),
219 Fabrice Barou (EBSD) and David Mainprice (MTEx coding). Travel was supported
220 by the Iveagh Fund, the LA-ICP-MS facility by SFI/12/ERC/E2499 and the FEG-
221 SEM by SFI/RI/3227.

FIGURE CAPTIONS

Figure 1: A) Scan of xenolith BP002 comprising orthopyroxene macrocryst with prominent garnet exsolution lamellae juxtaposed with a granular garnet harzburgite; B) Cross-polarized image of 200 μ m thin section showing strain birefringence and garnet inclusions in orthopyroxene. Boundary region between yellow lines.

Figure 2: (A) Photograph of (100) face of EBSD sample BP002 looking approx. down b axis, {110} cleavage is visible running NNW to SSE. (B) EBSD scatter pole figures of thin section shown in A showing axes to the {100}, {010} and {001} planes in orthopyroxene and axes to the {100} (faces), {111}, (space-diagonal planes) and {110} (face-diagonal) planes in garnet. (C) Schematic diagram showing the orientations of garnet lamellae (gray) in orthopyroxene (white), showing orthopyroxene cleavage on {110} (black lines). (D) Garnet fabric (axes in grey) within lamellae at an acute angle to orthopyroxene host (axes in black) on the (100) face of BP002 from (B).

Figure 3: Chondrite (McDonough and Sun, 1995) normalized trace element composition of phases in the megacrystic and granular portions of BP002, inset shows trace element data for Kimberley xenoliths from Simon et al. (2007).

Figure 4: Pressure-temperature diagram contoured for Al content of orthopyroxene (dashed grey, 100Al per 6 oxygens; Gasparik, 2000) showing the equilibration conditions of the megacryst (grey triangle), the precursor (grey line).

REFERENCES

- Aoki, K. I., Fujimaki, H. and Kitamura, M. (1980) 'Exsolved garnet-bearing pyroxene megacrysts from some South African kimberlites', *Lithos*, 13(3), pp. 269-279.
- Arndt, N. T., Coltice, N., Helmstaedt, H. and Gregoire, M. (2009) 'Origin of Archean subcontinental lithospheric mantle: Some petrological constraints', *Lithos*, 109(1-2), pp. 61-71.
- Bell, D. R., Gregoire, M., Grove, T. L., Chatterjee, N., Carlson, R. W. and Buseck, P. R. (2005) 'Silica and volatile-element metasomatism of Archean mantle: a xenolith-scale example from the Kaapvaal Craton', *Contributions to Mineralogy and Petrology*, 150(3), pp. 251-267.
- Boyd, F. R. (1989) 'Compositional distinction between oceanic and cratonic lithosphere', *Earth and Planetary Science Letters*, 96(1-2), pp. 15-26.
- Boyd, F. R. and Mertzman, S. A. (1987) 'Composition and structure of the Kaapvaal lithosphere, South Africa', in Mysen, B.O. (ed.) *Magmatic Processes: Physicochemical Principles*: The Geochemical Society, pp. 13-24.
- Brey, G. P., Kohler, T. and Nickel, K. G. (1990) 'Geothermobarometry in 4-phase lherzolites. 1. Experimental results from 10 to 60 kb', *Journal of Petrology*, 31(6), pp. 1313-1352.
- Canil, D. (1991) 'Experimental evidence for the exsolution of cratonic peridotite from high-temperature harzburgite', *Earth and Planetary Science Letters*, 106(1-4), pp. 64-72.
- Canil, D. (1992) 'Orthopyroxene stability along the peridotite solidus and the origin of cratonic lithosphere beneath South Africa', *Earth and Planetary Science Letters*, 111(1), pp. 83-95.

272 Canil, D. (2004) 'Mildly incompatible elements in peridotites and the origins of
 273 mantle lithosphere', *Lithos*, 77(1-4), pp. 375-393.

274 Chin, E. J., Lee, C. T. A. and Blichert-Toft, J. (2015) 'Growth of upper plate
 275 lithosphere controls tempo of arc magmatism: Constraints from Al-
 276 diffusion kinetics and coupled Lu-Hf and Sm-Nd chronology',
 277 *Geochemical Perspectives Letters*, 1(1), pp. 20-32.

278 Chin, E. J., Lee, C. T. A., Luffi, P. and Tice, M. (2012) 'Deep Lithospheric
 279 Thickening and Refertilization beneath Continental Arcs: Case Study of
 280 the P, T and Compositional Evolution of Peridotite Xenoliths from the
 281 Sierra Nevada, California', *Journal of Petrology*, 53(3), pp. 477-511.

282 Cox, K. G., Smith, M. R. and Beswetherick, S. (1987) 'Textural studies of garnet
 283 lherzolites: evidence of exsolution origin from high temperature
 284 harzburgites', in Nixon, P.H. (ed.) *Mantle Xenoliths*: Wiley, London, pp.
 285 537-550.

286 Dawson, J. B. (2004) 'A fertile harzburgite-gamet lherzolite transition: possible
 287 inferences for the roles of strain and metasomatism in upper mantle
 288 peridotites', *Lithos*, 77(1-4), pp. 553-569.

289 Dawson, J. B., Smith, J. V. and Hervig, R. L. (1980) 'Heterogeneity in upper-mantle
 290 lherzolites and harzburgites', *Philosophical Transactions of the Royal
 291 Society a-Mathematical Physical and Engineering Sciences*, 297(1431),
 292 pp. 323-+.

293 Dawson, J. B. and Stephens, W. E. (1975) 'Statistical classification of garnets from
 294 kimberlite and associated xenoliths', *Journal of Geology*, 83(5), pp. 589-
 295 607.

296 Gasparik, T. (2000) 'An internally consistent thermodynamic model for the system
 297 CaO-MgO-Al₂O₃-SiO₂ derived primarily from phase equilibrium data',
 298 *Journal of Geology*, 108(1), pp. 103-119.

299 Gibson, S. A. (2017) 'On the nature and origin of garnet in highly-refractory Archean
 300 lithospheric mantle: constraints from garnet exsolved in Kaapvaal craton
 301 orthopyroxenes', *Mineralogical Magazine*.

302 Griffin, W. L., O'Reilly, S. Y., Abe, N., Aulbach, S., Davies, R. M., Pearson, N. J.,
 303 Doyle, B. J. and Kivi, K. (2003) 'The origin and evolution of Archean
 304 lithospheric mantle', *Precambrian Research*, 127(1-3), pp. 19-41.

305 Harley, S. L. (1984) 'An experimental study of the effect of Ca upon garnet-
 306 clinopyroxene Fe-Mg exchange equilibria', *Contributions to Mineralogy
 307 and Petrology*, 86(4), pp. 359-373.

308 Herzberg, C. (2004) 'Geodynamic information in peridotite petrology', *Journal of
 309 Petrology*, 45(12), pp. 2507-2530.

310 Herzberg, C. T. (1993) 'Lithospheric peridotites in the Kaapvaal craton', *Earth and
 311 Planetary Science Letters*, 120(1-2), pp. 13-29.

312 Kelemen, P. B., Hart, S. R. and Bernstein, S. (1998) 'Silica enrichment in the
 313 continental upper mantle via melt/rock reaction', *Earth and Planetary
 314 Science Letters*, 164(1-2), pp. 387-406.

315 Malkovets, V. G., Griffin, W. L., O'Reilly, S. Y. and Wood, B. J. (2007) 'Diamond,
 316 subcalcic garnet, and mantle metasomatism: Kimberlite sampling patterns
 317 define the link', *Geology*, 35(4), pp. 339-342.

318 McDonough, W. F. and Sun, S. S. (1995) 'The composition of the Earth', *Chemical
 319 Geology*, 120(3-4), pp. 223-253.

320 Parman, S. W., Grove, T. L., Dann, J. C. and de Wit, M. J. (2004) 'A subduction
 321 origin for komatiites and cratonic lithospheric mantle', *South African*
 322 *Journal of Geology*, 107(1-2), pp. 107-118.

323 Pearson, D. G., Carlson, R. W., Shirey, S. B., Boyd, F. R. and Nixon, P. H. (1995)
 324 'Stabilisation of Archaean lithospheric mantle: A Re-Os isotope study of
 325 peridotite xenoliths from the Kaapvaal craton', *Earth and Planetary*
 326 *Science Letters*, 134(3-4), pp. 341-357.

327 Saltzer, R. L., Chatterjee, N. and Grove, T. L. (2001) 'The spatial distribution of
 328 garnets and pyroxenes in mantle peridotites: Pressure-temperature history
 329 of peridotites from the Kaapvaal craton', *Journal of Petrology*, 42(12), pp.
 330 2215-2229.

331 Shu, Q. and Brey, G. P. (2015) 'Ancient mantle metasomatism recorded in subcalcic
 332 garnet xenocrysts: Temporal links between mantle metasomatism,
 333 diamond growth and crustal tectonomagmatism', *Earth and Planetary*
 334 *Science Letters*, 418, pp. 27-39.

335 Simon, N. S. C., Carlson, R. W., Pearson, D. G. and Davies, G. R. (2007) 'The origin
 336 and evolution of the Kaapvaal cratonic lithospheric mantle', *Journal of*
 337 *Petrology*, 48(3), pp. 589-625.

338 Sobolev, N. V., Lavrent'ev, Y. G., Pokhilenko, N. P., Usova, L. V., 0.0px, p. p. m. p.
 339 p. p. and Calibri}, f. p. (1973) 'Chrome-rich garnets from kimberlites of
 340 Yakutia and their paragenesis', *Contributions to Mineralogy and*
 341 *Petrology*, 40(1), pp. 39-52.

342 Stachel, T., Viljoen, K. S., Brey, G. and Harris, J. W. (1998) 'Metasomatic processes
 343 in lherzolitic and harzburgitic domains of diamondiferous lithospheric

344 mantle: REE in garnets from xenoliths and inclusions in diamonds', *Earth*
345 *and Planetary Science Letters*, 159(1-2), pp. 1-12.

346 Walter, M. J. (1998) 'Melting of garnet peridotite and the origin of komatiite and
347 depleted lithosphere', *Journal of Petrology*, 39(1), pp. 29-60.

348 Wasch, L. J., van der Zwan, F. M., Nebel, O., Morel, M. L. A., Hellebrand, E. W. G.,
349 Pearson, D. G. and Davies, G. R. (2009) 'An alternative model for silica
350 enrichment in the Kaapvaal subcontinental lithospheric mantle',
351 *Geochimica Et Cosmochimica Acta*, 73(22), pp. 6894-6917.

352

Figure

[Click here to download Figure fig4_bw.png](#)

	Olivine			Garnet		
wt%	Xenolith	2 σ (n=9)	Xenolith	2 σ (n=33)	Megacryst	2 σ (n=21)
SiO ₂	41.59	0.59	42.41	0.23	41.73	0.71
Al ₂ O ₃	<LOD	-	21.26	0.27	21.91	0.89
Cr ₂ O ₃	<LOD	-	3.52	0.37	3.53	0.31
FeO	6.52	0.15	6.37	0.10	6.27	0.17
MnO	0.07	0.05	0.25	0.04	0.26	0.04
MgO	51.83	0.57	21.70	0.26	21.88	0.19
CaO		-	4.48	0.13	4.39	0.20
Mg#	93.4		85.9		86.2	
Ts (%)	-		-		-	
ppm				2 σ (n=10)		2 σ (n=7)
Sc	-	-	94	13	87	9
V	-	-	200	30	176	15
Cr	-	-	-	-	-	-
Mn	-	-	2478	177	2417	192
Co	-	-	41	5	42	5
Ni	-	-	40	6	39	3
Y	-	-	3.1	0.8	3.4	1.1
Zr	-	-	67	10	70	10
Nb	-	-	0.25	0.08	0.25	0.09
La	-	-	0.10	0.04	0.06	0.04
Ce	-	-	1.6	0.2	1.1	0.7
Pr	-	-	0.65	0.10	0.51	0.18
Nd	-	-	5.1	1.1	4.8	0.7
Sm	-	-	2.5	0.4	2.4	0.3
Eu	-	-	0.96	0.14	0.92	0.15
Gd	-	-	2.4	0.4	2.5	0.5
Dy	-	-	1.1	0.2	1.2	0.3
Ho	-	-	0.12	0.02	0.14	0.04
Er	-	-	0.21	0.05	0.22	0.07
Yb	-	-	0.15	0.02	0.15	0.03
Lu	-	-	0.03	0.01	0.03	0.01
Hf	-	-	0.91	0.16	0.97	0.11
Th	-	-	0.01	0.01	0.01	0.01
U	-	-	0.08	0.09	0.11	0.12

error is 2sd

Xenolith	Orthopyroxene		2σ ($N=26$)	Precursor Megacryst
	2σ ($n=30$)	Megacryst		
58.15	0.21	58.38	0.49	56.65
0.75	0.07	0.74	0.06	2.94
0.27	0.03	0.27	0.05	0.61
3.99	0.10	4.00	0.10	4.24
0.08	0.04	0.07	0.03	0.09
36.45	0.25	36.20	0.52	34.71
0.32	0.04	0.33	0.04	0.75
94.20		94.1		93.60
1.1		1.1		5.40
	2σ ($n=7$)		2σ ($n=6$)	
2.6	1.2	2.4	0.3	11.25
43	10	37	3	51.2
2070	322	1978	1316	-
631	139	631	99	817
50	10	50	5	49.2
801	123	766	206	691
0.009	0.002	0.010	0.004	0.37
0.38	0.09	0.41	0.06	7.70
0.16	0.03	0.13	0.01	0.14
0.010	0.003	0.006	0.001	0.011
0.053	0.017	0.038	0.009	0.146
0.013	0.004	0.011	0.003	0.063
0.085	0.021	0.067	0.005	0.558
0.026	0.004	0.024	0.004	0.270
0.008	0.001	0.007	0.001	0.102
0.016	0.005	0.016	0.002	0.276
0.005	0.001	0.004	0.001	0.131
0.000	0.000	0.000	0.000	0.015
<LOD	-	<LOD	-	-
<LOD	-	<LOD	-	-
<LOD	-	<LOD	-	-
0.013	0.006	0.013	0.003	0.113
0.001	0.001	0.001	0.001	0.002
0.001	0.001	0.001	0.001	0.012

P (GPa)	reference
4.37	Brey, G.P. & Koehler, T. (1990). Geothermobarometry in four-phase lherzolites II. I
4.12	Brey, G.P., Bulatov V.K. & Girnis A.V. (2008). Geobarometry for Peridotites: Exp
4.53	Nickel, K.G. & Green, D.H. (1985). Empirical geothermobarometry for garnet perid
4.50	MacGregor, I.D. (1974). The system MgO–Al ₂ O ₃ –SiO ₂ : solubility of Al ₂ O ₃ in ensta
4.04	Ryan, C. G., Griffin, W. L. & Pearson, N. J. (1996). Garnet geotherms: pressure–ten

New thermobarometers, and practical assessment of existing thermobarometers. *Journal of Petrology*, **49**, 1460-2415

Experiments in Simple and Natural Systems from 6 to 10 GPa. *Journal of Petrology*, **49**, 1460-2415

Peridotites and implications for the nature of the lithosphere, kimberlites and diamonds. *Earth Planetary Science Letters*, **100**, 439-456

Thermobarometry for spinel and garnet peridotite compositions. *American Mineralogist* **59**, 110-119.

Temperature data from Cr-pyroxene garnet xenocrysts in volcanic rocks. *Journal of Geophysical Research*, **94**, 10,387-10,400

gy **31**, 1353–1378.

y *Science Letters* **73**, 158–170.

ch **101**, 5611–5625.

ANALYTICAL METHODS

EBSD

Crystallographic orientation of garnet and orthopyroxene in the BP002 megacryst were determined on two near-perpendicular thin sections, which were highly polished and uncoated. Electron back-scatter diffraction (EBSD) patterns were collected using a JEOL 5600 SEM system equipped with a NORD LYS camera (hkl technology) at Geosciences Montpellier. The sample was positioned at a tilt angle 70° from horizontal within the SEM specimen chamber, and was analysed with a 30µm spot at a working distance of 24mm using a 17kV accelerating volt and a beam current of 37nA. Each pattern was indexed against Enstatite Opx AV77 and Pyrope 11 giving Mean Angular Deviations (MADs) of <0.7%. Data was collected using Oxford Instruments Aztec V2.4, and noise reduction was undertaken using HKL Tango using 6 nearest neighbor interpolation. Data processing was done using the MTEX free toolbox for Matlab (version 4.3.2; <http://mtex-toolbox.github.io>).

FGE-SEM-EDS

Major elements were analysed by Field Gun Emission Scanning Electron Microscope Energy Dispersive Spectrometry (FGE-SEM-EDS) at the iCRAG lab at Trinity College Dublin. Analyses was carried out using a Tescan TIGER MIRA3 Variable Pressure Field Emission Scanning Electron Microscope, equipped with two Oxford X-Max 80mm² detectors, using the Oxford AZtec X-ray microanalysis software. A beam current of ~285pA was used with an accelerating voltage of 20kV. The instrument was calibrated using a suite of appropriate mineral standards from the Smithsonian Institute (Jarosewich et al., 1980). Errors are reported as 2σ. Accuracies of 0.6%, 3.2%, and 1.1% were attained for the natural diopside reference mineral NMNH 117733 for SiO₂, MgO, and CaO respectively. *State-of-the-art field emission gun SEM systems with silicon drift EDX, when operated like electron microprobes, are capable of producing major element data of comparable quality to WDS systems (e.g. Newbury and Richie, 2015).*

LA-ICP-MS

Trace elements were analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Trinity College Dublin. The instrument used was a Teledyne Photon Machines Analyte G2 laser ablation system, comprising a 193nm ArF excimer laser and a HeLex II active two-volume ablation cell, coupled to a Thermo iCAPQc ICP-MS.

Routine analyses used 2.75Jcm^{-2} an $85\times 85\mu\text{m}$ spot size and a repetition rate of 80Hz for 2400 shots, with each ablation separated by 30s counting on the gas blank. The calibration standard was USGS GSD-1G, and USGS BHVO-2G, USGS GSA-1G and NIST616 were used as quality control standards. Rare earth element (REE) concentrations in orthopyroxene were determined using a $156\times 156\mu\text{m}$ spot size and a repetition rate of 80Hz for 4000 shots and 60s counting on the background, the total sweep time was 5s, following the method of (Stead et al., 2017). Care was taken to clean analyse grain interiors, free from fractures and inclusions. Data reduction was done using Iolite 2.5 using ^{29}Si as the internal standard. Errors are reported as 2σ . Accuracy is typically $<5\%$ for trace elements in USGS reference materials BHVO-G and GS-A.

Jarosewich, E., Nelen, J. A. and Norberg, J. (1980) 'Reference samples for electron microprobe analysis', *Geostandards Newsletter*, 4, pp. 43-47.

Newbury, D. E., and Ritchie, N. W. (2015) 'Performing elemental microanalysis with high accuracy and high precision by scanning electron microscopy/silicon drift detector energy-dispersive X-ray spectrometry (SEM/SDD-EDS)', *Journal of Materials Science*, 50(2), pp. 493-518.

Stead, C. V., Tomlinson, E. L., Kamber, B. S., Babechuk, M. G. and McKenna, C. A. (2017) 'Rare Earth Element Determination in Olivine by Laser Ablation-Quadrupole-ICP-MS: An Analytical Strategy and Applications', *Geostandards and Geoanalytical Research*, 41(2), pp. 197-212.

EBSD RESULTS

Garnet crystals have a fabric, with garnets in both lamellae populations having a dominant crystallographic axis orientation (Fig. 1). The topotactic relationship between the garnet and the host orthopyroxene is not simple, the garnet grains are orientated at an acute angle to orthopyroxene at $(072)_{\text{opx}}//(\text{021})_{\text{grt}}$, $(1351)_{\text{opx}}//(\text{862})_{\text{grt}}$, $(912)_{\text{opx}}//(\text{826})_{\text{grt}}$, $(612)_{\text{opx}}//(\text{627})_{\text{grt}}$, (Fig. 2).

Figure 1: EBSD scatter pole figures showing orientation of different crystallographic axes in the two orthogonal BP002 thin sections (figure 2E and 2F) rotated to look down the pole to the (001) plane of orthopyroxene. Low index surfaces of garnet in different crystals, different lamellae and different lamellae populations are aligned. Note, axes to the $\{100\}$ (faces), $\{111\}$, (space-diagonal planes) and $\{110\}$ (face-diagonal) planes of the garnet cube.

Figure 2: Inverse pole figure showing the orthopyroxene (green) and garnet (red) crystallographic planes corresponding to maxima in the preferred orientation of misorientation axes.

GEOCHEMISTRY RESULTS

Compositional halos around garnet lamellae

Minor compositional zoning is seen around garnet lamellae with Al₂O₃ increasing and SiO₂ decreasing towards garnet lamellae (Fig 1).

Figure 1: Gradients in Al₂O₃ and SiO₂ concentration in orthopyroxene around garnet lamellae (Errors are 2σ), data for regions opxrim1 to opxB1 in figure 1.

Trace element equilibration

There is good agreement between the measured garnet/orthopyroxene ratios and those predicted by partition coefficients both for the rare earth elements (Sun and Liang, 2013) and other trace elements (Salters et al, 2002).

Figure 2: Observed ‘vs’ predicted garnet/orthopyroxene ratios for the megacryst in BP002.

References

Salters, V.J.M., Longhi, J.E. and Bizimis, M. (2002) Near mantle solidus trace element partitioning at pressures up to 3.4GPa. *Geochemistry, Geophysics, Geosystems*, 3, DOI:10.1029/2001GC000148.

Sun, C. G. and Liang, Y. (2013) 'The importance of crystal chemistry on REE partitioning between mantle minerals (garnet, clinopyroxene, orthopyroxene, and olivine) and basaltic melts', *Chemical Geology*, 358, pp. 23-36.