Insights into the Mantle Geochemistry of Scandium from a Meta-Analysis of Garnet Data

Mathieu Chassé, William L Griffin, Olivier Alard, Suzanne Y. O'reilly,
Georges Calas

► To cite this version:

Mathieu Chassé, William L Griffin, Olivier Alard, Suzanne Y. O'reilly, Georges Calas. Insights into the Mantle Geochemistry of Scandium from a Meta-Analysis of Garnet Data. *Lithos*, 2018, 310-311, pp.409-421. 10.1016/j.lithos.2018.03.026 . hal-01910703

HAL Id: hal-01910703

<https://hal.science/hal-01910703>

Submitted on 1 Nov 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Insights into the Mantle Geochemistry of Scandium 2 from a Meta-Analysis of Garnet Data

3 Mathieu Chassé^{*,a,b}, William L. Griffin^b, Olivier Alard^{b,c}, Suzanne Y.
4 O'Reilly^b, Georges Calas^a

5 ^a*Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC),
6 Sorbonne Université, Muséum national d'Histoire naturelle, UMR CNRS 7590, IRD,
7 F-75005 Paris, France*

8 ^b*Australian Research Council Centre of Excellence for Core to Crust Fluid Systems
9 (CCFS) and GEMOC, Department of Earth and Planetary Sciences, Macquarie
10 University, NSW 2109, Australia*

11 ^c*Géosciences Montpellier, Université de Montpellier II, UMR CNRS 5243, 34095
12 Montpellier, France*

13 ^{*}*Corresponding author at: Institut de minéralogie, de physique des matériaux et de
14 cosmochimie, Sorbonne Université, 4 place Jussieu, case courrier 115, F-75005 Paris,
15 France.*

16 *E-mail address: mathieu.chasse@normalesup.org (M. Chassé).*

17 Abstract

18 The meta-analysis of about 13,000 analyses of scandium content in gar-
19 net grains shows that, below the spinel–garnet transition, this phase carries
20 about three-quarters of the Sc budget of the mantle, indicating its control on
21 Sc mobility. The Sc content of garnets in mafic rocks is low, due to a dilution
22 effect resulting from their high modal content in garnet. Garnets from ultra-
23 mafic rocks exhibit a wider range of Sc concentrations. We assess the relative
24 influence of thermobarometry, crystal chemistry and fluid-related events on
25 the distribution of Sc in garnet from such rocks to improve the tracking of
26 geochemical processes in the mantle. Pressure and temperature of equili-
27 bration in the mantle are second-order factors influencing the Sc content of
28 garnet, while crystal-chemistry, in particular $\frac{Cr}{Cr+Al}$ and $\frac{Ca}{Ca+Mg}$, is the main

parameter controlling the compatibility of Sc. Scandium is incorporated in both X and Y sites of Cr-Ca-rich garnets, resulting in a behaviour intermediate between rare-earth elements, incorporated in the X site, and trivalent transition elements, occupying the Y site. This affinity for both sites results in a mild compatibility of Sc in the garnet stability field of the mantle; hence Sc concentration in garnet increases with melt extraction and can be reduced by silicate-melt metasomatism. In contrast, metasomatism by volatile-rich fluids increases the Sc concentration in garnet. The control of garnet on the compatibility of Sc in deep lithospheric rocks demonstrates the potential of using Sc to track the conditions of formation of magmas and their residual rocks, as well as the origin and nature of metasomatic fluids.

Keywords: Crystal chemistry; Partitioning; Rare-earth elements; Melt extraction; Metasomatism; Volatile-rich fluids

1. Introduction

Scandium is a common trace element in the silicate Earth, with an average concentration of *ca* 16.4 ppm (Palme and O'Neill, 2014). It is the lightest first-row transition element, and is sometimes considered as a rare-earth element (REE; Connelly et al., 2005). Occurring only in the trivalent state, Sc is not affected by redox conditions and shows a lithophile behaviour (Samson and Chassé, 2016). During mantle melting, Sc is mildly incompatible, being enriched in the continental crust, arc magmas and mid-ocean ridge basalts (MORB) relative to the primitive mantle, but is believed not to be mobilised in other mantle-related fluids (Lee et al., 2005).

52

53 Based on the Geochemistry of Rocks of the Oceans and Continents (GEOROC)
54 database (Sarbas and Nohl, 2008), we show that Sc concentration varies by
55 one order of magnitude between Sc-poor ultramafic rocks and Sc-rich mafic
56 rocks (Fig. 1a). This selective concentration of Sc results from wide vari-
57 ations of its compatibility in rock-forming minerals (Fig. 1b). Typical Sc
58 concentrations in garnets are seven times higher than the estimate for the
59 silicate Earth, well above any other mineral group. The crystal chemistry and
60 trace-element patterns of mantle garnets record a great variety of geochemical
61 processes (Baxter et al., 2013), associated with mantle geochemistry (Wood
62 et al., 2013), metamorphism or tectonics (Caddick and Kohn, 2013). Garnet
63 from the subcontinental lithospheric mantle is a key indicator of fluid-related
64 events in the mantle (Griffin et al., 1999a) which may control Sc mobility be-
65 tween the shallow and deep regions of the upper mantle.

66
67 Trace-element concentration in garnet depends on site preference and
68 crystal-chemical mechanisms of incorporation as functions of pressure, tem-
69 perature and the chemical composition of the melt and solid phases present
70 during garnet formation. Despite the ability of garnet to incorporate signif-
71 icant amounts of Sc, such information is limited in natural contexts. The
72 discovery of a Sc-bearing garnet, eringaite ($\text{Ca}_3\text{Sc}_2(\text{SiO}_4)_3$; Galuskina et al.,
73 2010), the latest of the only eight natural Sc silicate minerals discovered on
74 Earth, demonstrates the affinity of Sc for the six-fold-coordinated Y site of
75 calcic garnets, already known in synthetic garnets by the existence of a solid
76 solution between andradite ($\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$) and eringaite (Quartieri et al.,
77 2006). However, in synthetic pyrope-grossular ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$)– $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$)

solid solutions (Oberti et al., 2006; Kim et al., 2007), the pyrope end-member preferentially incorporates Sc in the eight-fold-coordinated X site. Natural compositions of mantle garnets studied here are in the range $(\text{Mg}_{1-x-y}\text{Ca}_x\text{Fe}_y)_3(\text{Al}_{1-z}\text{Cr}_z)_2(\text{SiO}_4)_3$, with x in the range $[0.1, 0.25]$, y in the range $[0.1, 0.25]$ and z in the range $[0, 0.25]$, corresponding to an intermediate member of the pyrope–almandine–uvarovite $[(\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3)_{50}-(\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3)_{25}-(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3)_{25}]$ solid solution. The term garnet is used hereafter to cover this variability, of prime importance to understand Sc incorporation in this phase.

The objective of this paper is to study the influence of garnet on the geochemical behaviour of Sc, by gathering about 13,000 analyses of Sc content in mantle-related garnet representing about 600 different samples from 97 studies published over the last 50 years. Our statistical approach demonstrates the influence of host-rock composition, crystal chemistry, thermobarometric conditions and fluid-related events on Sc content in mantle-related garnet (hereafter $[\text{Sc}]_{\text{grt}}^1$). This discussion demonstrates that Sc may be used to trace geochemical events, including partial melting and metasomatism, occurring below the spinel–garnet transition zone.

2. Database and Methods

2.1. Constitution of the Database of Garnet Analyses

The database used for this work contains about 13,000 analyses on garnet grains, mostly obtained by laser ablation–inductively coupled plasma mass

¹More generally, $[\text{X}]_{\text{grt}}$ stands for the concentration of the element X in garnet.

100 spectrometry. Before 2000, some data were obtained by X-ray fluorescence,
 101 mass spectrometry and instrumental neutron activation analysis on separated
 102 garnets or using proton microprobe on garnet grains. All variables analysed
 103 in at least one publication are provided (Table A.1). More than 5500 anal-
 104 yses come from GEMOC/CCFS (see Griffin et al., 1999a, 2002). The other
 105 7500 garnet analyses were gathered from the GEOROC database (Sarbas
 106 and Nohl, 2008). Most analysed grains come from the subcontinental litho-
 107 spheric mantle and were extracted from ultramafic xenoliths or concentrates
 108 from kimberlites. A minor part consists of eclogitic garnets. The analysed
 109 minerals come from 165 localities worldwide (Table A.2). Apart from gar-
 110 net xenocrysts and megacrysts, for which the lithotype of the host-rock is
 111 unknown or not relevant, six categories have been selected to obtain sta-
 112 tistically representative subsets: eclogite, pyroxenite, lherzolite, peridotite,
 113 harzburgite and wehrnite. The peridotite category is used when the host-rock
 114 was not described more precisely. A few lithotypes, do not fall into any of
 115 these categories and have been left out. When the major-element chemistry
 116 of garnet was available, garnet xenocrysts have been subclassified (Grütter
 117 et al., 2004; Schulze, 2003).

118

119 Only variables contained in at least 70 % of the records have been used,
 120 leaving Si, Al, Cr, Fe, Mn, Mg and Ca as major- and minor elements and
 121 Ce, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Y and Sc as trace elements. Despite
 122 appearing in only 55 % of the records, Ti analyses have been kept to classify
 123 garnet xenocrysts. The database has been analysed using the R software
 124 (version 3.3.2, R Core Team, 2016). Details on the data analysis and the

125 statistical treatment of the database are given in Appendix A.

126

127 *2.2. Modelling the Influence of Mantle Melting on Scandium Concentrations*

128 To assess the validity of our analysis on the influence of partial melting
 129 on Sc behaviour, we used a model based on the experimental determination
 130 of Sc concentration during the melting of a near-pyrolitic mantle in the gar-
 131 net stability field from 3 GPa to 7 GPa (Walter, 1998). For each melting
 132 experiment, the modal proportions are calculated by mass balance between
 133 the composition of the coexisting phases and the bulk composition of the
 134 system at equilibrium (Walter, 1998).

135

136 Mass balance calculations provide Sc concentration in the melt and in the
 137 residue according to the following formula:

$$138 \quad [\text{Sc}]_{\text{melt}} = \frac{[\text{Sc}]_0}{D_{\text{Sc}}^{\text{res/melt}} \cdot (1 - F) + F} \quad (1)$$

139

$$140 \quad [\text{Sc}]_{\text{res}} = \frac{D_{\text{Sc}}^{\text{res/melt}} \cdot [\text{Sc}]_0}{D_{\text{Sc}}^{\text{res/melt}} \cdot (1 - F) + F} \quad (2)$$

141 where $[\text{Sc}]_0$ the concentration of Sc in the initial system, $[\text{Sc}]_{\text{res}}$ the Sc con-
 142 centration in the residue, $[\text{Sc}]_{\text{melt}}$ the Sc concentration in the melt, F the
 143 mass fraction of melt and $D_{\text{Sc}}^{\text{res/melt}}$ the partition coefficient of Sc between the
 144 residue and the melt. As the melt is in equilibrium with the different phases
 145 during batch melting experiments, $[\text{Sc}]_{\text{grt}}$ has been obtained as follows:

$$146 \quad [\text{Sc}]_{\text{grt}} = D_{\text{Sc}}^{\text{grt/melt}} \cdot [\text{Sc}]_{\text{melt}} \quad (3)$$

147 The starting Sc concentration ($[\text{Sc}]_0$) corresponds to a pyrolitic mantle (*ca* 16.4 ppm,
 148 Palme and O'Neill, 2014). The partition coefficients of Sc between the residue
 149 and the melt are obtained by summing Sc partition coefficients between each
 150 phase and the melt (Davis et al., 2013), weighted by the modal proportion
 151 of the phase considered. To our knowledge, this is the only study reporting
 152 together the partition coefficients of Sc for olivine, garnet and pyroxenes,
 153 applicable to partial melting of the mantle in the stability field of garnet.
 154 Variations in the range of deviations indicated in this study do not influence
 155 the results.

156 **3. Results**

157 *3.1. Scandium Distribution in Garnet and its Host-Rocks*

158 Garnet is the main rock-forming mineral incorporating Sc (Fig. 1b and
 159 Table A.3). Scandium concentrations in host-rocks are statistically higher in
 160 mafic than in ultramafic rocks (Fig. 1a, Tables A.3 and A.4). The Sc content
 161 in the host-rock decreases with the depletion in fusible components, but such
 162 differences are considered with care as they are not statistically significant
 163 (p -value > 0.05). A positive correlation exists between the Sc concentration
 164 in the host-rock and the proportion of Sc incorporated in garnet, indicating
 165 that *ca* 75 % of the Sc content of the host-rock is incorporated in garnet
 166 (Fig. 2a). Where studies from the dataset report the average Sc concentra-
 167 tion in garnet, in their host-rock and the modal garnet content of the host-
 168 rock, we have used these data to estimate the proportion of Sc incorporated
 169 by garnet for each lithotype; values are in the range of 65 % to 80 % (Fig. 2b).

170

171 The bimodal distribution of $[\text{Sc}]_{\text{grt}}$ is related to the nature of the host-
 172 rocks (Fig. 3). The low- $[\text{Sc}]_{\text{grt}}$ population, *ca* 50 ppm median, corresponds to
 173 mafic rocks: eclogites and pyroxenites. The main population, with a median
 174 $[\text{Sc}]_{\text{grt}}$ of *ca* 120 ppm corresponds to peridotitic rocks.

175

176 The nature of the host-rocks (Fig. 4 and Table A.5) and the class of the
 177 garnet xenocrysts (Schulze, 2003; Grütter et al., 2004) show that Sc concen-
 178 tration in peridotitic garnet increases with the degree of melt depletion in the
 179 host-rock, confirming the compatibility of Sc in mantle-derived garnet. The
 180 statistical significance of these observations is confirmed by ANOVA tests
 181 (Table A.6).

182

183 Garnets from mafic and ultramafic host-rocks form two distinct popula-
 184 tions in terms of $[\text{Sc}]_{\text{grt}}$. For later discussion, the dataset considered contains
 185 only analyses of garnets from peridotitic host-rocks, according to the descrip-
 186 tion of the host-rock and to the classification by Schulze (2003) in the case
 187 of xenocrysts.

188 *3.2. Relationships between Scandium Concentration and Thermobarometric* 189 *Parameters of the Mantle*

190 Garnets from ultramafic rocks equilibrated with mantle olivine, enabling
 191 the use of the nickel thermometer (T_{Ni} , Ryan et al., 1996) to investigate the
 192 role of temperature on the distribution of $[\text{Sc}]_{\text{grt}}$. No correlation exists be-
 193 tween T_{Ni} and $[\text{Sc}]_{\text{grt}}$ (Fig. 5a, Table A.7, p -value > 0.05). On the subset
 194 of data for which the thermobarometer of Brey and Köhler (1990) has been
 195 used to estimate the temperature (T_{BKN}) and pressure (P_{BKN}), there is no

196 correlation with $[\text{Sc}]_{\text{grt}}$ (Figs. 5b and c, Table A.7, p -value > 0.05).

197

198 3.3. Relationships between Scandium and Major-Element Concentrations

199 Scandium concentration in garnet is correlated with garnet major-element
200 chemistry (Fig. 6, Table A.8). The strongest positive correlation exists be-
201 tween $[\text{Sc}]_{\text{grt}}$ and $[\text{Cr}]_{\text{grt}}$ ($r = 0.43$, p -value < 0.05) while a negative correlation
202 exists between $[\text{Sc}]_{\text{grt}}$ and $[\text{Al}]_{\text{grt}}$ ($r = -0.35$, p -value < 0.05). A weaker posi-
203 tive correlation exists between $[\text{Sc}]_{\text{grt}}$ and $[\text{Ca}]_{\text{grt}}$ ($r = 0.28$, p -value < 0.05),
204 while a negative correlation is found between $[\text{Sc}]_{\text{grt}}$ and $[\text{Mg}]_{\text{grt}}$ ($r = -0.20$,
205 p -value < 0.05). Chromium and Al occupy the Y site of garnet while Ca and
206 Mg occupy the X site. These correlations confirm the influence of crystal
207 chemistry on the incorporation of Sc in natural garnets shown in experimen-
208 tal conditions by Oberti et al. (2006); Quartieri et al. (2006) and Kim et al.
209 (2007). However, $\text{Cr}\#$ ($\frac{[\text{Cr}]_{\text{grt}}}{[\text{Cr}]_{\text{grt}} + [\text{Al}]_{\text{grt}}}$) and $\text{Ca}\#$ ($\frac{[\text{Ca}]_{\text{grt}}}{[\text{Ca}]_{\text{grt}} + [\text{Mg}]_{\text{grt}}}$) are also indica-
210 tors of melt extraction from the host-rock. Therefore, correlations between
211 $[\text{Sc}]_{\text{grt}}$ and $[\text{Cr}]_{\text{grt}}$, $[\text{Al}]_{\text{grt}}$, $[\text{Ca}]_{\text{grt}}$ or $[\text{Mg}]_{\text{grt}}$ may also reflect the degree of de-
212 pletion of the host-rock (Fig. 7a).

213

214 Variations of $[\text{Sc}]_{\text{grt}}$ versus $[\text{Fe}]_{\text{grt}}$ show two main trends (Fig. 6), result-
215 ing in the apparent absence of statistical significance (p -value > 0.05). A
216 negative correlation exists at high $[\text{Fe}]_{\text{grt}}$, and a positive correlation at lower
217 $[\text{Fe}]_{\text{grt}}$ giving a low overall correlation ($r = 0.07$). This can be related to the
218 variable speciation of Fe: Fe^{2+} or Fe^{3+} incorporated in the X or Y site. The
219 fertility of the host-rock may also be involved, as shown by the decrease of
220 $[\text{Sc}]_{\text{grt}}$ with increasing $\frac{[\text{Mg}]_{\text{grt}}}{[\text{Mg}]_{\text{grt}} + [\text{Fe}]_{\text{grt}}}$ ($\text{Mg}\#$), an indicator of depletion (Fig. 7b).

221 A negative correlation between $[\text{Sc}]_{\text{grt}}$ and $[\text{Si}]_{\text{grt}}$ ($r = -0.24$, $p\text{-value} < 0.05$)
 222 is related to the correlations between $[\text{Si}]_{\text{grt}}$ and $[\text{Al}]_{\text{grt}}$, $[\text{Cr}]_{\text{grt}}$, $[\text{Mg}]_{\text{grt}}$ and
 223 $[\text{Ca}]_{\text{grt}}$. Silicon concentration in garnet is positively correlated with $[\text{Al}]_{\text{grt}}$
 224 and $[\text{Mg}]_{\text{grt}}$ and negatively correlated with $[\text{Cr}]_{\text{grt}}$ and $[\text{Ca}]_{\text{grt}}$ explaining the
 225 anticorrelation with $[\text{Sc}]_{\text{grt}}$. The lack of a correlation between $[\text{Sc}]_{\text{grt}}$ and
 226 $[\text{Mn}]_{\text{grt}}$ ($p\text{-value} > 0.05$) reflects the low $[\text{Mn}]_{\text{grt}}$ in the garnets studied, hin-
 227 dering any influence on garnet crystal chemistry.

228

229 3.4. Relationships between Scandium and Trace-Element Concentrations

230 Scandium concentration in garnet is positively correlated with the con-
 231 centration of light rare-earth elements (LREE, *e.g.*, $r = 0.28$ for Nd with
 232 a $p\text{-value} < 0.05$, Table A.9) and becomes negative for heavy rare-earth ele-
 233 ments and Y (HREE, *e.g.*, $r = -0.20$ for Yb with a $p\text{-value} < 0.05$, Table A.9,
 234 Fig. 8).

235

236 Plots of $[\text{Y}]_{\text{grt}}$ versus $[\text{Zr}]_{\text{grt}}$ provide a signature of melt depletion and
 237 metasomatism (Griffin et al., 1999b). Such plots (Fig. 9a), on which $[\text{Sc}]_{\text{grt}}$
 238 has been reported, confirm that garnets from depleted rocks are enriched in
 239 Sc compared to those in fertile ones, while indicators of metasomatism by
 240 silicate melt are weakly correlated with $[\text{Sc}]_{\text{grt}}$.

241

242 The variation of $(\text{Ce}/\text{Yb})_{\text{N}}$ versus $(\text{Zr}/\text{Sm})_{\text{N}}$ can be used to distinguish
 243 metasomatic processes related to volatile-rich fluids or to silicate melts (Aulbach
 244 et al., 2004). In our dataset, high $[\text{Sc}]_{\text{grt}}$ is associated with high $(\text{Ce}/\text{Yb})_{\text{N}}$,
 245 indicating that volatile-rich metasomatism positively affects $[\text{Sc}]_{\text{grt}}$ (Fig. 9b).

246 On the contrary, no correlation is visible between $[\text{Sc}]_{\text{grt}}$ and $(\text{Zr}/\text{Sm})_{\text{N}}$, con-
247 firming that metasomatism by silicate melts has a limited influence on $[\text{Sc}]_{\text{grt}}$.

248 3.5. Evolution of Scandium Concentration During Melting

249 The evolution of the Sc content in the residual rock, in the melt and
250 in the garnets is estimated from melting experiments on fertile peridotite
251 (Walter, 1998), as explained in the “Database and Methods” section. In
252 the presence of garnet and with increasing degree of partial melting, Sc con-
253 centration increases in the melt and decreases in the residue, whatever the
254 pressure (Figs. 10a and b). The comparison with the modal garnet content
255 (Fig. 10c) indicates that low modal proportions, which may result from melt-
256 ing, increase the Sc concentration in the melt and decrease Sc concentration
257 in the residue. The calculated values of $[\text{Sc}]_{\text{grt}}$ are consistent with the con-
258 centrations of the dataset, confirming the validity of this approach. With
259 increasing degree of partial melting, $[\text{Sc}]_{\text{grt}}$ increases by up to 100 ppm over
260 a range of partial melting representative of the mantle (Fig. 10d).

261 4. Discussion

262 4.1. Garnet, the Main Scandium Carrier in the Deep Lithospheric Mantle

263 At the depths considered in the dataset, between 70 km and 200 km,
264 garnet is the main host for Sc. It accounts for *ca* 75 % of the Sc budget of the
265 deep lithospheric mantle (Fig. 2a, regression curve), in agreement with the
266 proportion of Sc incorporated in various lithotypes of mantle-rocks (Fig. 1b).
267 Considering the median $[\text{Sc}]_{\text{grt}}$ from mafic and ultramafic rocks and estimates
268 of the modal content of garnet (Perrillat et al., 2006; Stixrude and Lithgow-
269 Bertelloni, 2007; Pearson et al., 2014), our estimate of the abundance of Sc

in the lithospheric mantle is consistent with those based on other methods (Table 1; Palme et al., 2014; Pearson et al., 2014; White and Buss, 2014), confirming that regardless of the context, garnet incorporates three-quarters of the Sc budget of the subcontinental lithospheric mantle. Such a constant high proportion, independent of the context, indicates that, in the presence of garnet, the mobility of Sc is controlled by this phase.

4.2. Dilution Effect

The low $[\text{Sc}]_{\text{grt}}$ in mafic host-rocks compared to ultramafic ones cannot be attributed to a compositional effect, as the median Sc content of mafic rocks (*ca* 40 ppm, Fig. 1c) is higher than that of ultramafic rocks (*ca* 10 ppm). This could reflect a lower compatibility of Sc in garnet from mafic parent rocks. However, experimentally-determined partition coefficients are inconsistent with this hypothesis: $D_{\text{Sc}}^{\text{grt/melt}} = 8.3$ for eclogitic garnet and $D_{\text{Sc}}^{\text{grt/melt}} = 6.0$ for peridotitic garnet (Pertermann et al., 2004; Davis et al., 2013, respectively). This difference must reflect a dilution effect due to the high modal garnet content of mafic rocks.

The rest of this discussion will focus on Sc concentration in garnets from ultramafic host-rocks, which constitute the major part of the dataset. The lower garnet contents of these rocks makes them insensitive to dilution effects.

4.3. Impact of Thermobarometric Conditions

Models of the dependence of $D_{\text{Sc}}^{\text{grt/melt}}$ on pressure, temperature and composition have been calibrated to experiments for the X site of garnet (van

293 Westrenen and Draper, 2007). However, the incorporation of Sc in mantle-
294 derived garnets is not correlated with pressure or temperature (Figs. 5a, b
295 and c), indicating the predominance of compositional effects.

296 4.4. *Impact of Melt Extraction*

297 Depletion of mantle peridotites by removal of mafic melts is correlated
298 with increased $[\text{Sc}]_{\text{grt}}$. Lherzolithic garnets (G9) have low $[\text{Sc}]_{\text{grt}}$ compared to
299 harzburgitic ones (G10; Figs. 4a and b) and $[\text{Sc}]_{\text{grt}}$ increases with Cr#, a
300 measure of depletion (Fig. 7). According to our estimates based on melting
301 experiments, $[\text{Sc}]_{\text{grt}}$ increases with melt extraction (Fig. 10d) in agreement
302 with the observations in natural garnets.

303
304 Nonetheless, at constant Cr#, $[\text{Sc}]_{\text{grt}}$ decreases with increasing Mg# or
305 decreasing Ca# (Fig. 7), two indicators of depletion of the host-rock. Vari-
306 ations of $D_{\text{Sc}}^{\text{grt/melt}}$ thus cannot be explained by melt-extraction only, and
307 changes in crystal chemistry must be invoked. The correlations between
308 $[\text{Sc}]_{\text{grt}}$ and Cr# also imply crystal-chemical effects, considering that this pa-
309 rameter reflects the nature of the atoms occupying the Y-site.

310 4.5. *Impact of Garnet Crystal Chemistry*

311 Correlations between Sc and major elements (Fig 6) indicate the affinity
312 of Sc for the uvarovite end-member of garnet ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$), indicating the
313 significance of Cr in the crystal chemistry of mantle garnet. Although often
314 referred to as a minor element, it can hardly be considered as such when it
315 commonly reaches 0.5 apfu. In Cr-rich systems, the crystal-chemical mecha-
316 nisms of Sc incorporation are unknown and $D_{\text{Sc}}^{\text{grt/melt}}$ has not been determined

317 experimentally, but experimental studies on garnet crystal-chemistry provide
 318 likely explanations on the influence of Cr. When the uvarovite component
 319 is limited, the composition is close to pyrope and Sc is mainly incorporated
 320 in the X site of garnet (Oberti et al., 2006). When the composition shifts
 321 toward the grossular end-member, with Cr content remaining low, the relax-
 322 ation of the garnet structure by substitution of Mg^{2+} ($r(\text{VIII}\text{Mg}^{2+}) = 0.89 \text{ \AA}$,
 323 Shannon, 1976) for the larger cation Ca^{2+} ($r(\text{VIII}\text{Ca}^{2+}) = 1.12 \text{ \AA}$) results in
 324 an enlargement of both X and Y sites (Oberti et al., 2006; Kim et al., 2007)
 325 and increases the incorporation of Sc in these sites. However, in grossular,
 326 the size of the Y octahedron is constrained by the sole presence of the small
 327 Al^{3+} cation ($r(\text{VI}\text{Al}^{3+}) = 0.54 \text{ \AA}$), limiting the incorporation of Sc in the Y
 328 site (Oberti et al., 2006). When Sc substitutes for the larger Fe^{3+} ion in the
 329 high-spin state (Lin and Wheat, 2012, $r(\text{VI}\text{Fe}^{3+}, \text{high spin}) = 0.65 \text{ \AA}$) along
 330 the join andradite–eringaite, this barrier is removed, and Sc is incorporated
 331 exclusively in the Y site (Quartieri et al., 2006). Iron(III) has an ionic radius
 332 of similar to Cr^{3+} ($r(\text{VI}\text{Cr}^{3+}) = 0.62 \text{ \AA}$). By analogy, when the uvarovite
 333 component is significant, the less compact structure of Cr-Ca-rich garnet
 334 thus will favour the incorporation of Sc in the Y site. Large Y octahedra
 335 occupied by Cr and locally related to X dodecahedra occupied by Ca should
 336 coexist with small Y octahedra occupied by Al close to X dodecahedra oc-
 337 cupied by Mg. Because Ca can reach 1.5 apfu, the result should be a highly
 338 strained structure. In these compositions, Sc might predominantly enter a
 339 highly deformed Y site close to X sites occupied by Mg, helping to reduce
 340 the strain because this X site is large compared to the one in pyrope.

341

342 This incorporation of Sc in the Y site of Ca-Cr-rich garnet is consistent
 343 with lattice-strain theory (Wood and Blundy, 2014), which relates the charge
 344 and radius of an ion to its partition coefficient in the crystallographic site
 345 of a given mineral species at a given temperature and pressure. From this
 346 theory and the experimental determination of trace-element partition coefficients,
 347 Onuma diagrams (Onuma et al., 1968) have been retrieved (Fig. 11)
 348 for mantle-related garnet end-members at thermobarometric conditions representative
 349 of the mantle (Corgne and Wood, 2004; Dasgupta et al., 2009; Corgne et al., 2012).
 350 Scandium is less compatible in the X or Y sites of the pyrope end-member than in the
 351 grossular end-member (Fig. 11a). The Onuma diagram expected from the interpretation
 352 given above is presented for the Y site for the uvarovite end-member as experimental data
 353 are not available. As explained above, incorporation of Cr and Ca in the garnet
 354 structure expands the Y site, increasing the compatibility of Sc in this site
 355 (Fig. 11b). This has a prominent effect on the variability of $[\text{Sc}]_{\text{grt}}$. As Sc
 356 compatibility in the Y site is low in pyrope, even a small expansion of the Y
 357 site can dramatically increase Sc compatibility.
 358

359
 360 This interpretation is consistent with the relationships between $[\text{Sc}]_{\text{grt}}$ and
 361 $[\text{REE}]_{\text{grt}}$. Scandium is positively correlated with LREE and negatively with
 362 HREE (Fig. 8). The small ionic radius of Sc should make it more comparable
 363 to a HREE in terms of compatibility in the X site of garnet (Fig. 11a).
 364 However, the decrease in $[\text{Sc}]_{\text{grt}}$ with increasing $[\text{HREE}]_{\text{grt}}$ indicates that the
 365 compatibility of Sc in garnet falls as the compatibility of HREE increases.
 366 This can only be explained by the incorporation of part of the Sc in the Y site

367 of garnet, while other HREE remain incompatible in the Y site of Cr-Ca-rich
 368 garnets (Fig. 11b). The shift towards the incorporation of Sc in the Y site
 369 of garnet tracks an enlargement of the X site of garnet, increasing the com-
 370 patibility of LREE and explaining the positive correlation with Sc, while the
 371 effect on the compatibility of HREE remains limited. The incorporation of
 372 Sc in the Y site may also explain the poor correlation between $[\text{Sc}]_{\text{grt}}$ and the
 373 temperature and pressure of equilibration of garnet; a complex relationship
 374 depending on both X and Y sites could blur any existing trend.

375

376 The variability of $[\text{Sc}]_{\text{grt}}$ in our database is mainly related to the capacity
 377 of the Y site of garnet to accept Sc. The X site may play a lesser role in
 378 constraining the partition coefficient of Sc for natural ranges of compositions.
 379 However, spectroscopic studies of Sc or experimental data on the partition
 380 coefficients of trace elements in the Y site of Cr-Ca-rich garnet are needed
 381 to quantify these effects.

382

383 4.6. *Impact of Metasomatic Processes*

384 Metasomatism of previously depleted rocks by silicate melts is not asso-
 385 ciated with variations in $[\text{Sc}]_{\text{grt}}$ (Fig. 9a). According to our melting model,
 386 Sc is mildly compatible in garnet-bearing mantle rocks. The Sc content of
 387 silicate melts is close from that of a garnet peridotite and $[\text{Sc}]_{\text{grt}}$ is not influ-
 388 enced by silicate-melt metasomatism. However, depleted garnets can reach
 389 high $[\text{Sc}]_{\text{grt}}$. A slight decrease in $[\text{Sc}]_{\text{grt}}$ exists along the silicate-melt metaso-
 390 matism trend (from bright red to dark purple spots, Fig. 9a). In that case,
 391 the difference in Sc concentration between the garnet and the metasomatic

392 melt is great enough to lead to a decrease in $[\text{Sc}]_{\text{grt}}$.

393

394 Metasomatism by volatile-rich fluids is correlated with higher $[\text{Sc}]_{\text{grt}}$ (Fig. 9b),
395 contrasting with the low mobility expected for Sc in fluids from the shal-
396 low lithospheric mantle (Lee et al., 2005). This behaviour is expected for
397 strongly-incompatible elements (McKenzie, 1989; Bedini et al., 1997) but Sc
398 is compatible in the garnet stability field of the mantle. Two mechanisms
399 could explain the influence of volatile-rich fluids on $[\text{Sc}]_{\text{grt}}$. (i) At mantle
400 pressures and temperatures, complexing of Sc by volatile elements trans-
401 ports significant amounts of Sc and drastically decreases its compatibility.
402 This hypothesis is consistent with the occurrence of several Sc-rich carbon-
403 atites (up to 190 ppm Sc in whole-rock analyses, see *e.g.* Gramaccioli et al.,
404 2000). However, few data are available on Sc-complexes in fluids except for
405 hydrothermal fluids (Wood and Samson, 2006). Experiments indicate that
406 $D_{\text{Sc}}^{\text{grt}/\text{fluid}}$ increases from silicate to carbonate-rich melts (Fig. 11a, Dasgupta
407 et al., 2009). In the presence of garnet, carbonate-rich melts should not
408 transport significant amounts of Sc compared to other melts. (ii) The sec-
409 ond mechanism relies on the differences of compatibility between fertile and
410 depleted garnet, which is not modified during metasomatism by volatile-rich
411 fluids, as the fluids produced involve low volumes of melting ($< 1\%$, McKen-
412 zie, 1989). Volatile-rich fluids may be generated at the base of the lithosphere
413 (McKenzie, 1989; Bedini et al., 1997). In this context, the deeper lithosphere
414 is more fertile than in the upper parts, and consequently is richer in Sc
415 (Fig. 10). Scandium is also mildly compatible due to the lower $D_{\text{Sc}}^{\text{grt}/\text{melt}}$ of
416 fertile garnets compared to depleted ones. In this way, volatile-rich fluids can

417 be enriched in Sc compared to a depleted mantle. When these fluids ascend
 418 in the lithosphere and reach depleted parts of the mantle, the high compat-
 419 ibility of Sc in depleted garnets and the relatively high Sc concentration of
 420 the fluid combine to increase $[\text{Sc}]_{\text{grt}}$.

421 4.7. Validation of the Meta-Analysis on Selected Case Studies

422 **Impact of crystal chemistry.** Metasomatic events during the evolution
 423 of the subcontinental lithospheric mantle beneath the Siberian craton were
 424 inferred from peridotite xenoliths by Howarth et al. (2014). On the basis of
 425 the trends observed in the $\text{CaO-Cr}_2\text{O}_3$ diagram, increasing $[\text{Ca}]_{\text{grt}}$ at con-
 426 stant $[\text{Cr}]_{\text{grt}}$ is associated with a metasomatic refertilisation of harzburgite to
 427 lherzolite (Fig. 12a, arrow 1). Comparison with $[\text{Sc}]_{\text{grt}}$ shows that harzbur-
 428 gitic garnets have high $[\text{Sc}]_{\text{grt}}$ and refertilisation is associated with increasing
 429 $[\text{Sc}]_{\text{grt}}$. Increased $[\text{Ca}]_{\text{grt}}$ at constant $[\text{Cr}]_{\text{grt}}$ increases Sc compatibility in gar-
 430 net explaining the increased $[\text{Sc}]_{\text{grt}}$ during this first stage of metasomatism.
 431 The second stage is attributed to metasomatism by a kimberlitic melt, a
 432 product of small-degree partial melting (Fig. 12a, arrow 2). This event is
 433 associated with a decrease of $[\text{Sc}]_{\text{grt}}$, from *ca* 150 ppm to *ca* 100 ppm, typi-
 434 cal of lherzolithic garnet, and a decrease in $[\text{Ca}]_{\text{grt}}$ and $[\text{Cr}]_{\text{grt}}$, decreasing Sc
 435 compatibility in garnet. The third stage of metasomatism is associated with
 436 the percolation of extensive amounts of basaltic fluids (Fig. 12a, arrow 3).
 437 It is also associated with the strongest decrease of $[\text{Sc}]_{\text{grt}}$, from *ca* 150 ppm
 438 to *ca* 50 ppm. This metasomatic event led to complete re-equilibration of
 439 garnet and increased modal garnet content, explaining the decrease in $[\text{Sc}]_{\text{grt}}$.

440

441 Peridotite xenoliths from the Western Kaapvaal Craton show three groups

442 of garnets: low- and high-Cr lherzolitic garnets and harzburgitic garnets,
 443 characterised by the shape of their REE patterns and distinct La versus
 444 Cr/Ca ratio diagrams (Gibson et al., 2008). Figure 12b shows these three
 445 groups in the Sc versus Cr/Ca plot. According to Gibson et al. (2008), the
 446 high content of LREE, such as La, in harzburgitic garnet results from an
 447 enlargement of the X site. This is linked with the distortion of the crystal
 448 network caused by the substitution of Cr for Al, similar to the enhanced
 449 incorporation of Sc in the Cr-substituted Y site of harzburgitic garnet. This
 450 explains why La and Sc behave similarly with respect to Cr/Ca ratio, even
 451 though, Sc is closer in ionic radius to HREE than to LREE. This analogy
 452 between HREE and Sc leads us to suggest that the sinuous REE patterns
 453 of harzburgitic garnets reflect a partial incorporation of the heaviest REE in
 454 the Y site of Cr-rich harzburgitic garnet. In this case, the incorporation of
 455 both LREE and HREE in garnet is favoured by increasing $[\text{Cr}]_{\text{grt}}$ while such
 456 effects are limited for the middle-REE, between Gd and Er, which are not
 457 affected by the enlargement of the X site nor by the possibility of incorpora-
 458 tion in the Y site. This would explain the low concentration of middle-REE
 459 in REE patterns of harzburgitic garnet observed by Gibson et al. (2008).

460

461 **Impact of metasomatism.** Metasomatic events were proposed in the
 462 lithospheric mantle beneath the Canadian Shield, based on the geochemistry
 463 of xenoliths and xenocrysts from the Buffalo Hills kimberlite (Aulbach et al.,
 464 2004). The enrichment of incompatible elements in garnet and clinopyrox-
 465 ene was used to argue for an early stage of volatile-rich fluid metasomatism.
 466 In the Y–Zr diagram (Fig. 12c), most samples show high $[\text{Sc}]_{\text{grt}}$, between

467 *ca* 150 ppm and *ca* 250 ppm, regardless of the degree of depletion in terms of
 468 major elements. Volatile-rich metasomatism increases $[\text{Sc}]_{\text{grt}}$, explaining the
 469 disconnect between the degree of depletion and $[\text{Sc}]_{\text{grt}}$. The Y–Zr diagram
 470 also suggests the effects of silicate-melt metasomatism. Samples affected by
 471 this type of metasomatism exhibit a decrease in $[\text{Sc}]_{\text{grt}}$ (blue spots, Fig. 12c).
 472 This confirms that, when garnets are originally Sc-rich, silicate melt metasoma-
 473 tism can be seen in variations of $[\text{Sc}]_{\text{grt}}$.

474
 475 Metasomatic processes were investigated in the lithospheric mantle be-
 476 neath the Siberian craton (Agashev et al., 2013). The difference between
 477 the concentration of incompatible elements calculated from modal mineral-
 478 ogy and those measured was interpreted as reflecting the presence of cryptic
 479 phases induced by volatile-rich fluids during the formation of the garnet-
 480 bearing xenoliths. In the $(\text{Zr}/\text{Sm})_{\text{N}}-(\text{Ce}/\text{Yb})_{\text{N}}$ diagram (Fig. 12d), we ob-
 481 serve an increase in $[\text{Sc}]_{\text{grt}}$ associated with increasing $(\text{Ce}/\text{Yb})_{\text{N}}$ at low $(\text{Zr}/\text{Sm})_{\text{N}}$.
 482 This trend is compatible with the influence of volatile-rich metasomatism on
 483 $[\text{Sc}]_{\text{grt}}$, showing that the signature of this metasomatic stage is preserved by
 484 $[\text{Sc}]_{\text{grt}}$ despite later stages of silicate metasomatism and Fe-rich metasoma-
 485 tism described by Agashev et al. (2013).

487 5. Conclusions

488 This meta-analysis and statistical dissection of a large database of garnet
 489 compositions provides new information on the geochemistry of Sc in the
 490 deep lithospheric mantle and a basis for using $[\text{Sc}]_{\text{grt}}$ as a tracer of mantle

491 processes:

- 492 1. Garnet accounts for about 75 % of the Sc budget of the deep litho-
493 spheric mantle, regardless of the context, thus controlling the mobility
494 of Sc in the mantle.
- 495 2. High modal garnet contents in mafic rocks lead to dilution $[\text{Sc}]_{\text{grt}}$, lead-
496 ing to a specific geochemical behaviour of Sc in such host-rocks.
- 497 3. Melt extraction increases $[\text{Sc}]_{\text{grt}}$ showing the compatibility of this ele-
498 ment in the presence of garnet.
- 499 4. Crystal chemistry is the major parameter controlling $[\text{Sc}]_{\text{grt}}$. In partic-
500 ular, higher Cr# and Ca# in garnet increase the compatibility of Sc
501 in this phase.
- 502 5. Metasomatism has limited effect on $[\text{Sc}]_{\text{grt}}$ except in the specific case
503 of volatile-rich fluids, which can greatly enhance $[\text{Sc}]_{\text{grt}}$.

504 These conclusions and the selection of case studies show how Sc geochem-
505 istry can help recognise fluid-related processes in the mantle. Scandium is
506 mildly incompatible above the spinel–garnet transition zone (Mallmann and
507 O'Neill, 2009) while this study shows that Sc behaves as a mildly compatible
508 element in the garnet stability field. This unique behaviour results from the
509 ability of this element to enter both X and Y sites of Cr-Ca-rich garnets,
510 at the boundary between trivalent transition elements, which enter the Y
511 site, and REE, which occupy the X site. This behaviour reflects the singular
512 crystal chemistry of garnet from the lithospheric mantle, and emphasises the
513 need for experimental studies on partitioning of trace elements in Cr-Ca-rich
514 garnets. The balance between the variable compatibility of Sc in garnet,

515 depending on Cr# and Ca# and the modal garnet content of the host-rock
516 induces subtle variations in compatibility which can have drastic effects on Sc
517 contents, as shown by the unexpected effect of volatile-rich fluids on $[\text{Sc}]_{\text{grt}}$.
518 In well-constrained contexts, studying Sc concentration will help to under-
519 stand the conditions of generation of magmas, as well as the nature of their
520 residues.

521 **Declaration of Interest**

522 None.

523 **Acknowledgements**

524 We thank Mr Pierre Chassé and Dr Max Frenzel for fruitful discussions
525 and help on statistical methods. The authors are indebted to Dr Roberta
526 Oberti, Prof Douglas Smith and Dr Andrew Kerr for their comments and
527 suggestions which helped to improve this manuscript. Mathieu Chassé has
528 been supported by scholarships from the École normale supérieure (ENS)
529 and Macquarie University. Olivier Alard is supported by an Australian Re-
530 search Council grant (FT150100115). This work was funded by the Institut
531 universitaire de France (IUF) and a Foundation Grant from the ARC Centre
532 of Excellence for Core to Crust Fluid Systems (CCFS). This is contribu-
533 tion 1156 from the ARC Centre of Excellence for Core to Crust Fluid Sys-
534 tems (<http://www.ccfs.mq.edu.au>) and 1222 from the GEMOC Key Centre
535 (<http://www.gemoc.mq.edu.au>).

536 **References**

- 537 Agashev, A. M., Ionov, D. A., Pokhilenko, N. P., Golovin, A. V.,
538 Cherepanova, Y., Sharygin, I. S., 2013. Metasomatism in Lithospheric
539 Mantle Roots: Constraints from Whole-Rock and Mineral Chemical
540 Composition of Deformed Peridotite Xenoliths from Kimberlite Pipe
541 Udachnaya. *Lithos* 160-161, 201–215.
- 542 Appleyard, C. M., Bell, D. R., le Roex, A. P., 2007. Petrology and Geo-
543 chemistry of Eclogite Xenoliths from the Rietfontein Kimberlite, Northern
544 Cape, South Africa. *Contributions to Mineralogy and Petrology* 154, 309–
545 333.
- 546 Aulbach, S., Griffin, W. L., O'Reilly, S. Y., McCandless, T. E., 2004. Gen-
547 esis and Evolution of the Lithospheric Mantle Beneath the Buffalo Head
548 Terrane, Alberta (Canada). *Lithos* 77, 413–451.
- 549 Aulbach, S., Viljoen, K. S., 2015. Eclogite Xenoliths from the Lace Kimber-
550 lite, Kaapvaal Craton: from Convecting Mantle Source to Palaeo-Ocean
551 Floor and Back. *Earth and Planetary Science Letters* 431, 274–286.
- 552 Baxter, E. F., Caddick, M. J., Ague, J. J., 2013. Garnet: Common Mineral,
553 Uncommonly Useful. *Elements* 9, 415–419.
- 554 Bedini, R.-M., Bodinier, J.-L., Dautria, J.-M., Morten, L., 1997. Evolution
555 of LILE-Enriched Small Melt Fractions in the Lithospheric Mantle: a Case
556 Study from the East African Rift. *Earth and Planetary Science Letters*
557 153, 67–83.

- 558 Brey, G. P., Köhler, T., 1990. Geothermobarometry in Four-Phase Lher-
559 zolites II. New Thermobarometers, and Practical Assessment of Existing
560 Thermobarometers. *Journal of Petrology* 31, 1353–1378.
- 561 Caddick, M. J., Kohn, M. J., 2013. Garnet: Witness to the Evolution of
562 Destructive Plate Boundaries. *Elements* 9, 427–432.
- 563 Connelly, N. G., Damhus, T., Hartshorn, R. M., Hutton, A. T., 2005. Nomen-
564 clature of Inorganic Chemistry: IUPAC Recommendations 2005. The Royal
565 Society of Chemistry, Cambridge, United Kingdom.
- 566 Corgne, A., Armstrong, L. S., Keshav, S., Fei, Y., McDonough, W. F., Mi-
567 narik, W. G., Moreno, K., 2012. Trace Element Partitioning Between Ma-
568 joritic Garnet and Silicate Melt at 10–17 GPa: Implications for Deep Man-
569 tle Processes. *Lithos* 148, 128–141.
- 570 Corgne, A., Wood, B. J., 2004. Trace Element Partitioning Between Majoritic
571 Garnet and Silicate Melt at 25 GPa. *Physics of the Earth and Planetary*
572 *Interiors* 143, 407–419.
- 573 Dasgupta, R., Hirschmann, M. M., McDonough, W. F., Spiegelman, M.,
574 Withers, A. C., 2009. Trace Element Partitioning Between Garnet Lher-
575 zolite and Carbonatite at 6.6 and 8.6 GPa With Applications to the Geo-
576 chemistry of the Mantle and of Mantle-Derived Melts. *Chemical Geology*
577 262, 57–77.
- 578 Davis, F. A., Humayun, M., Hirschmann, M. M., Cooper, R. S., 2013. Exper-
579 imentally Determined Mineral/Melt Partitioning of First-Row Transition

- 580 Elements (FRTE) During Partial Melting of Peridotite at 3 GPa. *Geochim-*
581 *ica et Cosmochimica Acta* 104, 232–260.
- 582 Galuskina, I. O., Galuskin, E. V., Lazic, B., Armbruster, T., Dzierżanowski,
583 P., Prusik, K., Wrzalik, R., 2010. Eringaite, $\text{Ca}_3\text{Sc}_2(\text{SiO}_4)_3$, a New Mineral
584 of the Garnet Group. *Mineralogical Magazine* 74, 365–373.
- 585 Gibson, S. A., Malarkey, J., Day, J. A., 2008. Melt Depletion and Enrichment
586 Beneath the Western Kaapvaal Craton: Evidence from Finsch Peridotite
587 Xenoliths. *Journal of Petrology* 49, 1817–1852.
- 588 Gramaccioli, C. M., Diella, V., Demartin, F., 2000. The Formation of Scan-
589 dium Minerals As an Example of the Role of Complexes in the Geochem-
590 istry of Rare Earths and HFS Elements. *European Journal of Mineralogy*
591 12, 795–808.
- 592 Grégoire, M., Bell, D. R., Le Roex, A. P., 2003. Garnet Lherzolites from the
593 Kaapvaal Craton (South Africa): Trace Element Evidence for a Metaso-
594 matic History. *Journal of Petrology* 44, 629–657.
- 595 Griffin, W. L., Fisher, N. I., Friedman, J. H., O'Reilly, S. Y., Ryan, C. G.,
596 2002. Cr-Pyrope Garnets in the Lithospheric Mantle 2. Compositional Pop-
597 ulations and Their Distribution in Time and Space. *Geochemistry, Geo-*
598 *physics, Geosystems* 3, 1073.
- 599 Griffin, W. L., Fisher, N. I., Friedman, J. H., Ryan, C. G., O'Reilly, S. Y.,
600 1999a. Cr-Pyrope Garnets in the Lithospheric Mantle. I. Compositional
601 Systematics and Relations to Tectonic Settings. *Journal of Petrology* 40,
602 679–704.

603 Griffin, W. L., Shee, S. R., Ryan, C. G., Win, T. T., Wyatt, B. A., 1999b.
604 Harzburgite to Lherzolite and Back Again: Metasomatic Processes in
605 Ultramafic Xenoliths from the Wesselton Kimberlite, Kimberley, South
606 Africa. *Contributions to Mineralogy and Petrology* 134, 232–250.

607 Grütter, H. S., Gurney, J. J., Menzies, A. H., Winter, F., 2004. An Updated
608 Classification Scheme for Mantle-Derived Garnet, for Use by Diamond
609 Explorers. *Lithos* 77, 841–857.

610 Howarth, G. H., Barry, P. H., Pernet-Fisher, J. F., Baziotis, I. P., Pokhilenko,
611 N. P., Pokhilenko, L. N., Bodnar, R. J., Taylor, L. A., Agashev, A. M.,
612 2014. Superplume Metasomatism: Evidence from Siberian Mantle Xeno-
613 liths. *Lithos* 184-187, 209–224.

614 Ionov, D. A., 2004. Chemical Variations in Peridotite Xenoliths from Vitim,
615 Siberia: Inferences for REE and Hf Behaviour in the Garnet-Facies Upper
616 Mantle. *Journal of Petrology* 45, 343–367.

617 Jacob, D. E., Bizimis, M., Salters, V. J. M., 2005. Lu-Hf and Geochemical
618 Systematics of Recycled Ancient Oceanic Crust: Evidence from Roberts
619 Victor Eclogites. *Contributions to Mineralogy and Petrology* 148, 707–720.

620 Kim, N., Stebbins, J. F., Quartieri, S., Oberti, R., 2007. Scandium-45 NMR
621 of Pyrope-Grossular Garnets: Resolution of Multiple Scandium Sites and
622 Comparison With X-Ray Diffraction and X-Ray Absorption Spectroscopy.
623 *American Mineralogist* 92, 1875–1880.

624 Lee, C.-T. A., Leeman, W. P., Canil, D., Li, Z.-X. A., 2005. Similar V/Sc
625 Systematics in MORB and Arc Basalts: Implications for the Oxygen Fu-

- 626 gacities of Their Mantle Source Regions. *Journal of Petrology* 46, 2313–
627 2336.
- 628 Lin, J.-F., Wheat, A., 2012. Electronic Spin Transition of Iron in the Earth’s
629 Lower Mantle. *Hyperfine Interactions* 207, 81–88.
- 630 Mallmann, G., O’Neill, H. S. C., 2009. The Crystal/Melt Partitioning of
631 V During Mantle Melting As a Function of Oxygen Fugacity Compared
632 With Some Other Elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb).
633 *Journal of Petrology* 50, 1765–1794.
- 634 McDonough, W. F., Sun, S. s., 1995. The Composition of the Earth. *Chemical*
635 *Geology* 120, 223–253.
- 636 McKenzie, D., 1989. Some Remarks on the Movement of Small Melt Fractions
637 in the Mantle. *Earth and Planetary Science Letters* 95, 53–72.
- 638 Oberti, R., Quartieri, S., Dalconi, M. C., Boscherini, F., Iezzi, G., Boiocchi,
639 M., Eeckhout, S. G., 2006. Site Preference and Local Geometry of Sc in
640 Garnets: Part I. Multifarious Mechanisms in the Pyrope-Grossular Join.
641 *American Mineralogist* 91, 1230–1239.
- 642 Onuma, N., Higuchi, H., Wakita, H., Nagasawa, H., 1968. Trace Element
643 Partition Between Two Pyroxenes and the Host Lava. *Earth and Planetary*
644 *Science Letters* 5, 47–51.
- 645 Palme, H., Lodders, K., Jones, A., 2014. Solar System Abundances of the El-
646 ements, in: Holland, H., Turekian, K. K. (Eds.), *Treatise on Geochemistry*,
647 2nd Edition, Elsevier Ltd., Amsterdam, the Netherlands, pp. 15–36.

- 648 Palme, H., O'Neill, H., 2014. Cosmochemical Estimates of Mantle Composi-
649 tion, in: Holland, H., Turekian, K. K. (Eds.), Treatise on Geochemistry,
650 2nd Edition, Elsevier Ltd., Amsterdam, the Netherlands, pp. 1–39.
- 651 Pearson, D. G., Canil, D., Shirey, S. B., 2014. Mantle Samples Included in
652 Volcanic Rocks: Xenoliths and Diamonds, in: Holland, H., Turekian, K. K.
653 (Eds.), Treatise on Geochemistry, 2nd Edition, Elsevier Ltd., Amsterdam,
654 the Netherlands, pp. 170–253.
- 655 Perrillat, J.-P., Ricolleau, A., Daniel, I., Fiquet, G., Mezouar, M., Guignot,
656 N., Cardon, H., 2006. Phase Transformations of Subducted Basaltic Crust
657 in the Upmost Lower Mantle. *Physics of the Earth and Planetary Interiors*
658 157, 139–149.
- 659 Pertermann, M., Hirschmann, M. M., Hametner, K., Gülnther, D., Schmidt,
660 M. W., 2004. Experimental Determination of Trace Element Partitioning
661 Between Garnet and Silica-Rich Liquid During Anhydrous Partial Melt-
662 ing of MORB-Like Eclogite. *Geochemistry, Geophysics, Geosystems* 5,
663 Q05A01.
- 664 Quartieri, S., Oberti, R., Boiocchi, M., Dalconi, M. C., Boscherini, F., Sa-
665 fonova, O., Woodland, A. B., 2006. Site Preference and Local Geometry
666 of Sc in Garnets: Part II. the Crystal-Chemistry of Octahedral Sc in the
667 Andradite – $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ Join. *American Mineralogist* 91, 1240–1248.
- 668 R Core Team, 2016. R: a Language and Environment for Statistical Com-
669 puting. R Foundation for Statistical Computing, Vienna, Austria.

- 670 Ryan, C. G., Griffin, W. L., Pearson, N. J., 1996. Garnet Geotherms:
671 Pressure-Temperature Data from Cr-Pyrope Garnet Xenocrysts in Vol-
672 canic Rocks. *Journal of Geophysical Research* 101, 5611–5625.
- 673 Samson, I. M., Chassé, M., 2016. Scandium, in: White, W. M. (Ed.),
674 Encyclopedia of Geochemistry, Springer International Publishing, Cham,
675 Switzerland, pp. 1–5.
- 676 Sarbas, M., Nohl, U., 2008. The GEOROC Database As Part of a Growing
677 Geoinformatics Network, in: Geoinformatics Conference, Postdam, Ger-
678 many. Geological Society of America, pp. 3–4.
- 679 Schmickler, B., Jacob, D. E., Foley, S. F., 2004. Eclogite Xenoliths from the
680 Kuruman Kimberlites, South Africa: Geochemical Fingerprinting of Deep
681 Subduction and Cumulate Processes. *Lithos* 75, 173–207.
- 682 Schulze, D. J., 2003. A Classification Scheme for Mantle-Derived Garnets in
683 Kimberlite: a Tool for Investigating the Mantle and Exploring for Dia-
684 monds. *Lithos* 71, 195–213.
- 685 Shannon, R. D., 1976. Revised Effective Ionic Radii and Systematic Studies
686 of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallo-*
687 *graphica Section A: Foundations and Advances* A32, 751–767.
- 688 Stixrude, L., Lithgow-Bertelloni, C., 2007. Influence of Phase Transforma-
689 tions on Lateral Heterogeneity and Dynamics in Earth’s Mantle. *Earth*
690 *and Planetary Science Letters* 263, 45–55.
- 691 Ulianov, A., Kalt, A., Pettke, T., 2006. Aluminous Websterite and Granulite
692 Xenoliths from the Chyulu Hills Volcanic Field, Kenya: Gabbro-Troctolitic

- 693 Cumulates Subjected to Lithospheric Foundering. *Contributions to Min-*
694 *eralogy and Petrology* 152, 459–483.
- 695 van Achterbergh, E., Griffin, W. L., Stiefenhofer, J., 2001. Metasomatism in
696 Mantle Xenoliths from the Letlhakane Kimberlites: Estimation of Element
697 Fluxes. *Contributions to Mineralogy and Petrology* 141, 397–414.
- 698 van Westrenen, W., Draper, D. S., 2007. Quantifying Garnet-Melt Trace
699 Element Partitioning Using Lattice-Strain Theory: New Crystal-Chemical
700 and Thermodynamic Constraints. *Contributions to Mineralogy and Petrol-*
701 *ogy* 154, 717–730.
- 702 Walter, M. J., 1998. Melting of Garnet Peridotite and the Origin of Komatiite
703 and Depleted Lithosphere. *Journal of Petrology* 39, 29–60.
- 704 White, A. F., Buss, H. L., 2014. Natural Weathering Rates of Silicate Min-
705 erals, in: Holland, H., Turekian, K. K. (Eds.), *Treatise on Geochemistry*,
706 2nd Edition, Elsevier Ltd., Amsterdam, the Netherlands, pp. 115–155.
- 707 Wood, B. J., Blundy, J. D., 2014. Trace Element Partitioning: the Influences
708 of Ionic Radius, Cation Charge, Pressure, and Temperature, in: Holland,
709 H., Turekian, K. K. (Eds.), *Treatise on Geochemistry*, 2nd Edition, Elsevier
710 Ltd., Amsterdam, the Netherlands, pp. 422–448.
- 711 Wood, B. J., Kiseeva, E. S., Matzen, A. K., 2013. Garnet in the Earth’s
712 Mantle. *Elements* 9, 421–426.
- 713 Wood, S. A., Samson, I. M., 2006. The Aqueous Geochemistry of Gallium,
714 Germanium, Indium and Scandium. *Ore Geology Reviews* 28, 57–102.

715 **Figure Captions**

716 Figure 1: Distribution of Sc concentration in minerals and mantle-related
717 rocks: (a) box-and-whisker plots of Sc concentration in selected mantle-
718 related rocks. The grey horizontal line corresponds to 16.4 ppm, the average
719 Sc concentration in the silicate Earth (Palme et al., 2014); (b) box-and-
720 whisker plots of Sc concentration in major rock-forming minerals. The box
721 is limited by the first and third quartiles of the data distribution. The hor-
722 izontal line represents the median, and the width of the adjacent notches
723 shows the 95 % confidence interval about the median. Where absent, this in-
724 terval is narrower than the thickness of the line representing the median. The
725 “whiskers” represent the last value before 1.5 times midrange (the arithmetic
726 mean of maximum and minimum values) beyond the first or third quartile.

728 Figure 2: Influence of host-rock parameters on $[\text{Sc}]_{\text{grt}}$: (a) scatter plot of
 729 Sc concentration in the host-rock versus the estimated Sc content in the
 730 host-rock attributable to garnet. This estimate is calculated using the $[\text{Sc}]_{\text{grt}}$
 731 and the modal content of garnet in the host-rock; (b) average proportion
 732 of Sc incorporated in the different mineral phases of garnet-bearing lherzo-
 733 lites, harzburgites, pyroxenites and eclogites (n: number of individual rocks
 734 analysed; after the only studies of the database reporting the required in-
 735 formation: van Achterbergh et al., 2001; Grégoire et al., 2003; Ionov, 2004;
 736 Schmickler et al., 2004; Jacob et al., 2005; Ulianov et al., 2006; Appleyard
 737 et al., 2007; Gibson et al., 2008; Aulbach and Viljoen, 2015). Values of Sc con-
 738 centration are sometimes absent for olivine and orthopyroxene grains, they
 739 are replaced by the median value calculated from the other studies reporting
 740 this content.

742 Figure 3: Density plot of $[\text{Sc}]_{\text{grt}}$ and histograms of $[\text{Sc}]_{\text{grt}}$ from mafic host-
 743 rock, fertile ultramafic host-rocks and depleted ultramafic host-rocks.

745 Figure 4: Variations in the distribution of $[\text{Sc}]_{\text{grt}}$ with the lithology of the
 746 host-rock: (a) box-and-whisker plots of $[\text{Sc}]_{\text{grt}}$ relative to the lithotype of the
 747 host-rock described in the original publications; (b) box-and-whisker plots
 748 of $[\text{Sc}]_{\text{grt}}$ in xenocrysts classified according to Grütter et al. (2004) (Xen.:
 749 all xenocryst values, G0: unclassified, G1: low-Cr megacrysts, G3: eclogitic,
 750 G5: pyroxenitic, G9: lherzolitic, G10: harzburgitic, G11: Ti-metasomatised,
 751 G12: wehrlitic). The box is limited by the first and third quartiles of the
 752 data distribution. The horizontal line represents the median, and the width
 753 of the adjacent notches shows the 95 % confidence interval about the median.
 754 Where absent, this interval is narrower than the thickness of the line repre-
 755 senting the median. The “whiskers” represent the last value before 1.5 times
 756 midrange (the arithmetic mean of maximum and minimum values) beyond
 758 the first or third quartile.

759 Figure 5: Influence of temperature and pressure on $[\text{Sc}]_{\text{grt}}$: (a) scatter plot
 760 of T_{Ni} (Ryan et al., 1996) versus $[\text{Sc}]_{\text{grt}}$; (b) scatter plot of T_{BKN} (Brey and
 761 Köhler, 1990) versus $[\text{Sc}]_{\text{grt}}$; (c) scatter plot of P_{BKN} (Brey and Köhler, 1990)
 763 versus $[\text{Sc}]_{\text{grt}}$. Estimates of T_{BKN} and P_{BKN} are from the original publications.

764 Figure 6: Correlation matrix and scatter plots for $[\text{Sc}]_{\text{grt}}$ versus major and
765 minor elements. Positive (respectively negative) correlations are indicated
766 by red (respectively blue) colours and the orientation of the ellipse. The
767 intensity of the correlation is given by the intensity of the colour (see colour
768 bar) and the narrowness of the ellipse.

770 Figure 7: Scatter plots of $[\text{Sc}]_{\text{grt}}$ relative to the ratios of selected major ele-
771 ments: (a) $\text{Cr}\#$ versus $\text{Ca}\#$; (b) $\text{Cr}\#$ versus $\text{Mg}\#$. The colour of each point
772 depends on the Sc content of the record, from 0 ppm (in blue) to 300 ppm
773 (in red).

775 Figure 8: Correlation matrix and scatter plots for $[\text{Sc}]_{\text{grt}}$ versus REE. Positive
776 (respectively negative) correlations are indicated by red (respectively blue)
777 colour and the direction of the ellipse. The intensity of the correlation is
778 given by the intensity of the colour (see colour bar) and the narrowness of
780 the ellipse.

781 Figure 9: Scatter plots of Sc relationships to trace-element indicators of
782 fluid-related processes in the mantle: (a) $[Y]_{\text{grt}}$ versus $[Zr]_{\text{grt}}$, the fields are
783 after Griffin et al. (1999b); (b) $(\text{Ce/Yb})_{\text{N}}$ versus $(\text{Zr/Sm})_{\text{N}}$, ratios have been
784 normalised to the values of McDonough and Sun (1995). The metasomatic
785 trends are after Aulbach et al. (2004). The colour of each point depends on
786 the Sc content of the record, from 0 ppm (in blue) to 300 ppm (in red).

788 Figure 10: Influence of partial melting of a fertile ultramafic mantle esti-
789 mated from Walter (1998) experiments: (a) evolution of the Sc content of
790 the residue; (b) evolution of the Sc content of the melt; (c) evolution of the
792 modal garnet content; (d) evolution of $[\text{Sc}]_{\text{grt}}$.

793 Figure 11: Onuma diagrams (Onuma et al., 1968) showing the partition
794 coefficients of trace elements as a function of their ionic radius: (a) X site of
795 garnet (Prp: pyrope, Grs: grossular); (b) Y site of garnet (Maj: majoritic
796 pyrope, Uv: uvarovite). Diagrams for the X site after van Westrenen and
797 Draper (2007) and Dasgupta et al. (2009); diagram for the Y site of majoritic
798 pyrope is from Corgne and Wood (2004) and an expected curve for the Y site
800 of uvarovite is given to illustrate the influence of Cr and Ca incorporation.

801 Figure 12: Evolution of $[\text{Sc}]_{\text{grt}}$ with garnet composition in selected case stud-
 802 ies: (a) evolution of $[\text{Sc}]_{\text{grt}}$ (given by the colour of each point) in the $\text{CaO}-$
 803 Cr_2O_3 diagram for garnets from the subcontinental lithospheric mantle be-
 804 neath the Siberian craton (Hz: harzburgitic garnet, Lz: lherzolitic garnet).
 805 The arrows represent three stages of metasomatism, described by Howarth
 806 et al. (2014); (b) distinction of garnet groups from the Kaapvaal craton de-
 807 pending on their relative Sc contents and Cr/Ca ratios; data are from Gibson
 808 et al. (2008); (c) evolution of $[\text{Sc}]_{\text{grt}}$ (given by the colour of each point) in the
 809 Y–Zr diagram for garnets from the Buffalo Head Terrane (Dep.: depleted);
 810 data are Aulbach et al. (2004), and the fields are from Griffin et al. (1999b);
 811 (d) evolution of $[\text{Sc}]_{\text{grt}}$ (given by the colour of each point) in the $(\text{Zr}/\text{Sm})_{\text{N}}-$
 812 $(\text{Ce}/\text{Yb})_{\text{N}}$ diagram for garnets from the Siberian craton, data from Agashev
 813 et al. (2013). The metasomatic trends are after Aulbach et al. (2004).

815 **Table Caption**

816 Table 1: Comparisons of Sc concentration in the mantle calculated from this
817 study with estimates from the literature for different mantle compositions.
818 The references used for each value are given in the table. The estimated Sc
819 concentration for this study is obtained using the following formula: $[\text{Sc}]_{\text{grt}} * \text{Mod} / 0.75$, with Mod the modal garnet content, $[\text{Sc}]_{\text{grt}}$ the median concen-
820 tration of Sc in the type of garnet considered and 0.75 our assessment of the
821 proportion of the Sc content in the mantle that is incorporated in garnet.
823