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

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► **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-01910703v1>

Submitted on 1 Nov 2018

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

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

42 **1. Introduction**

43 Scandium is a common trace element in the silicate Earth, with an aver-
44 age concentration of *ca* 16.4 ppm (Palme and O'Neill, 2014). It is the lightest
45 first-row transition element, and is sometimes considered as a rare-earth ele-
46 ment (REE; Connelly et al., 2005). Occurring only in the trivalent state, Sc
47 is not affected by redox conditions and shows a lithophile behaviour (Samson
48 and Chassé, 2016). During mantle melting, Sc is mildly incompatible, being
49 enriched in the continental crust, arc magmas and mid-ocean ridge basalts
50 (MORB) relative to the primitive mantle, but is believed not to be mobilised
51 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 ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$)– $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$)

78 solid solutions (Oberti et al., 2006; Kim et al., 2007), the pyrope end-member
79 preferentially incorporates Sc in the eight-fold-coordinated X site. Natural
80 compositions of mantle garnets studied here are in the range $(\text{Mg}_{1-x-y}\text{Ca}_x\text{Fe}_y)_3(\text{Al}_{1-z}\text{Cr}_z)_2(\text{SiO}_4)_3$,
81 with x in the range [0.1, 0.25], y in the range [0.1, 0.25] and z in the
82 range [0, 0.25], corresponding to an intermediate member of the pyrope50–
83 almandine25–uvarovite25 $[(\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3)50-(\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3)25-(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3)25]$
84 solid solution. The term garnet is used hereafter to cover this variability, of
85 prime importance to understand Sc incorporation in this phase.

86

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

96 **2. Database and Methods**

97 *2.1. Constitution of the Database of Garnet Analyses*

98 The database used for this work contains about 13,000 analyses on garnet
99 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 wehrlite. 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 -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 -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 -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 -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

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

276 *4.2. Dilution Effect*

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

286

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

290 *4.3. Impact of Thermobarometric Conditions*

291 Models of the dependence of $D_{\text{Sc}}^{\text{grt/melt}}$ on pressure, temperature and com-
292 position 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 coeffi-
347 cients, Onuma diagrams (Onuma et al., 1968) have been retrieved (Fig. 11)
348 for mantle-related garnet end-members at thermobarometric conditions rep-
349 resentative of the mantle (Corgne and Wood, 2004; Dasgupta et al., 2009;
350 Corgne et al., 2012). Scandium is less compatible in the X or Y sites of
351 the pyrope end-member than in the grossular end-member (Fig. 11a). The
352 Onuma diagram expected from the interpretation given above is presented
353 for the Y site for the uvarovite end-member as experimental data are not
354 available. As explained above, incorporation of Cr and Ca in the garnet
355 structure expands the Y site, increasing the compatibility of Sc in this site
356 (Fig. 11b). This has a prominent effect on the variability of $[\text{Sc}]_{\text{grt}}$. As Sc
357 compatibility in the Y site is low in pyrope, even a small expansion of the Y
358 site can dramatically increase Sc compatibility.

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 compara-
363 ble 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 metaso-
473 matism 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).

486

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.cafs.mq.edu.au>) and 1222 from the GEMOC Key Centre
535 (<http://www.gemoc.mq.edu.au>).

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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: lherzolithic, 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) Cr# versus Ca#; (b) Cr# versus 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) $(\text{Ce}/\text{Yb})_{\text{N}}$ versus $(\text{Zr}/\text{Sm})_{\text{N}}$, 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 CaO–
803 Cr₂O₃ 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 (Zr/Sm)_N–
812 (Ce/Yb)_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