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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

Abstract

The meta-analysis of about 13,000 analyses of scandium content in garnet grains shows that, below the spinel–garnet transition, this phase carries about three-quarters of the Sc budget of the mantle, indicating its control on Sc mobility. The Sc content of garnets in mafic rocks is low, due to a dilution effect resulting from their high modal content in garnet. Garnets from ultramafic rocks exhibit a wider range of Sc concentrations. We assess the relative influence of thermobarometry, crystal chemistry and fluid-related events on the distribution of Sc in garnet from such rocks to improve the tracking of geochemical processes in the mantle. Pressure and temperature of equilibration in the mantle are second-order factors influencing the Sc content of 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).
Based on the Geochemistry of Rocks of the Oceans and Continents (GEOROC) database (Sarbas and Nohl, 2008), we show that Sc concentration varies by one order of magnitude between Sc-poor ultramafic rocks and Sc-rich mafic rocks (Fig. 1a). This selective concentration of Sc results from wide variations of its compatibility in rock-forming minerals (Fig. 1b). Typical Sc concentrations in garnets are seven times higher than the estimate for the silicate Earth, well above any other mineral group. The crystal chemistry and trace-element patterns of mantle garnets record a great variety of geochemical processes (Baxter et al., 2013), associated with mantle geochemistry (Wood et al., 2013), metamorphism or tectonics (Caddick and Kohn, 2013). Garnet from the subcontinental lithospheric mantle is a key indicator of fluid-related events in the mantle (Griffin et al., 1999a) which may control Sc mobility between the shallow and deep regions of the upper mantle.

Trace-element concentration in garnet depends on site preference and crystal-chemical mechanisms of incorporation as functions of pressure, temperature and the chemical composition of the melt and solid phases present during garnet formation. Despite the ability of garnet to incorporate significant amounts of Sc, such information is limited in natural contexts. The discovery of a Sc-bearing garnet, eringaite (Ca$_3$Sc$_2$(SiO$_4$)$_3$; Galuskina et al., 2010), the latest of the only eight natural Sc silicate minerals discovered on Earth, demonstrates the affinity of Sc for the six-fold-coordinated Y site of calcic garnets, already known in synthetic garnets by the existence of a solid solution between andradite (Ca$_3$Fe$_2$(SiO$_4$)$_3$) and eringaite (Quartieri et al., 2006). However, in synthetic pyrope–grossular (Mg$_3$Al$_2$(SiO$_4$)$_3$–Ca$_3$Al$_2$(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 pyrope50–almandine25–uvarovite25 \([(\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3)_{50}–(\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3)_{25}–(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3)_{25}]\) 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

\(^1\)More generally, \([X]_{\text{grt}}\) stands for the concentration of the element X in garnet.
spectrometry. Before 2000, some data were obtained by X-ray fluorescence, mass spectrometry and instrumental neutron activation analysis on separated garnets or using proton microprobe on garnet grains. All variables analysed in at least one publication are provided (Table A.1). More than 5500 analyses come from GEMOC/CCFS (see Griffin et al., 1999a, 2002). The other 7500 garnet analyses were gathered from the GEOROC database (Sarbas and Nohl, 2008). Most analysed grains come from the subcontinental lithospheric mantle and were extracted from ultramafic xenoliths or concentrates from kimberlites. A minor part consists of eclogitic garnets. The analysed minerals come from 165 localities worldwide (Table A.2). Apart from garnet xenocrysts and megacrysts, for which the lithotype of the host-rock is unknown or not relevant, six categories have been selected to obtain statistically representative subsets: eclogite, pyroxenite, lherzolite, peridotite, harzburgite and wehrlite. The peridotite category is used when the host-rock was not described more precisely. A few lithotypes, do not fall into any of these categories and have been left out. When the major-element chemistry of garnet was available, garnet xenocrysts have been subclassified (Grütter et al., 2004; Schulze, 2003).

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

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

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

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

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

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

\[
[\text{Sc}]_{\text{grt}} = D_{\text{Sc}}^{\text{grt/melt}} \cdot [\text{Sc}]_{\text{melt}}
\]
The starting Sc concentration ([Sc]₀) corresponds to a pyrolitic mantle \((ca 16.4 \text{ ppm, Palme and O’Neill, 2014})\). The partition coefficients of Sc between the residue and the melt are obtained by summing Sc partition coefficients between each phase and the melt (Davis et al., 2013), weighted by the modal proportion of the phase considered. To our knowledge, this is the only study reporting together the partition coefficients of Sc for olivine, garnet and pyroxenes, applicable to partial melting of the mantle in the stability field of garnet. Variations in the range of deviations indicated in this study do not influence the results.

3. Results

3.1. Scandium Distribution in Garnet and its Host-Rocks

Garnet is the main rock-forming mineral incorporating Sc (Fig. 1b and Table A.3). Scandium concentrations in host-rocks are statistically higher in mafic than in ultramafic rocks (Fig. 1a, Tables A.3 and A.4). The Sc content in the host-rock decreases with the depletion in fusible components, but such differences are considered with care as they are not statistically significant \((p\text{-value } > 0.05)\). A positive correlation exists between the Sc concentration in the host-rock and the proportion of Sc incorporated in garnet, indicating that \(ca 75\ \%\) of the Sc content of the host-rock is incorporated in garnet (Fig. 2a). Where studies from the dataset report the average Sc concentration in garnet, in their host-rock and the modal garnet content of the host-rock, we have used these data to estimate the proportion of Sc incorporated by garnet for each lithotype; values are in the range of 65\% to 80\% (Fig. 2b).
The bimodal distribution of $[\text{Sc}]_{\text{grt}}$ is related to the nature of the host-rocks (Fig. 3). The low-$[\text{Sc}]_{\text{grt}}$ population, ca 50 ppm median, corresponds to mafic rocks: eclogites and pyroxenites. The main population, with a median $[\text{Sc}]_{\text{grt}}$ of ca 120 ppm corresponds to peridotitic rocks.

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

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

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

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

3.3. Relationships between Scandium and Major-Element Concentrations

Scandium concentration in garnet is correlated with garnet major-element chemistry (Fig. 6, Table A.8). The strongest positive correlation exists between $[\text{Sc}]_{\text{grt}}$ and $[\text{Cr}]_{\text{grt}}$ ($r = 0.43$, $p$-value < 0.05) while a negative correlation exists between $[\text{Sc}]_{\text{grt}}$ and $[\text{Al}]_{\text{grt}}$ ($r = -0.35$, $p$-value < 0.05). A weaker positive correlation exists between $[\text{Sc}]_{\text{grt}}$ and $[\text{Ca}]_{\text{grt}}$ ($r = 0.28$, $p$-value < 0.05), while a negative correlation is found between $[\text{Sc}]_{\text{grt}}$ and $[\text{Mg}]_{\text{grt}}$ ($r = -0.20$, $p$-value < 0.05). Chromium and Al occupy the Y site of garnet while Ca and Mg occupy the X site. These correlations confirm the influence of crystal chemistry on the incorporation of Sc in natural garnets shown in experimental conditions by Oberti et al. (2006); Quartieri et al. (2006) and Kim et al. (2007). However, Cr# (\frac{[\text{Cr}]_{\text{grt}}}{[\text{Cr}]_{\text{grt}}+ [\text{Al}]_{\text{grt}}}) and Ca# (\frac{[\text{Ca}]_{\text{grt}}}{[\text{Ca}]_{\text{grt}}+ [\text{Mg}]_{\text{grt}}}) are also indicators of melt extraction from the host-rock. Therefore, correlations between $[\text{Sc}]_{\text{grt}}$ and $[\text{Cr}]_{\text{grt}}$, $[\text{Al}]_{\text{grt}}$, $[\text{Ca}]_{\text{grt}}$ or $[\text{Mg}]_{\text{grt}}$ may also reflect the degree of depletion of the host-rock (Fig. 7a).

Variations of $[\text{Sc}]_{\text{grt}}$ versus $[\text{Fe}]_{\text{grt}}$ show two main trends (Fig. 6), resulting in the apparent absence of statistical significance ($p$-value > 0.05). A negative correlation exists at high $[\text{Fe}]_{\text{grt}}$, and a positive correlation at lower $[\text{Fe}]_{\text{grt}}$ giving a low overall correlation ($r = 0.07$). This can be related to the variable speciation of Fe: Fe$^{2+}$ or Fe$^{3+}$ incorporated in the X or Y site. The fertility of the host-rock may also be involved, as shown by the decrease of $[\text{Sc}]_{\text{grt}}$ with increasing $\frac{[\text{Mg}]_{\text{grt}}}{[\text{Mg}]_{\text{grt}}+ [\text{Fe}]_{\text{grt}}}$ (Mg#), an indicator of depletion (Fig. 7b).
A negative correlation between $[\text{Sc}]_{\text{grrt}}$ and $[\text{Si}]_{\text{grrt}}$ ($r = -0.24$, $p$-value $< 0.05$) is related to the correlations between $[\text{Si}]_{\text{grrt}}$ and $[\text{Al}]_{\text{grrt}}$, $[\text{Cr}]_{\text{grrt}}$, $[\text{Mg}]_{\text{grrt}}$ and $[\text{Ca}]_{\text{grrt}}$. Silicon concentration in garnet is positively correlated with $[\text{Al}]_{\text{grrt}}$ and $[\text{Mg}]_{\text{grrt}}$ and negatively correlated with $[\text{Cr}]_{\text{grrt}}$ and $[\text{Ca}]_{\text{grrt}}$ explaining the anticorrelation with $[\text{Sc}]_{\text{grrt}}$. The lack of a correlation between $[\text{Sc}]_{\text{grrt}}$ and $[\text{Mn}]_{\text{grrt}}$ ($p$-value $> 0.05$) reflects the low $[\text{Mn}]_{\text{grrt}}$ in the garnets studied, hindering any influence on garnet crystal chemistry.

### 3.4. Relationships between Scandium and Trace-Element Concentrations

Scandium concentration in garnet is positively correlated with the concentration of light rare-earth elements (LREE, $e.g.$, $r = 0.28$ for Nd with a $p$-value $<0.05$, Table A.9) and becomes negative for heavy rare-earth elements and Y (HREE, $e.g.$, $r = -0.20$ for Yb with a $p$-value $<0.05$, Table A.9, Fig. 8).

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

The variation of $(\text{Ce/Yb})_N$ versus $(\text{Zr/Sm})_N$ can be used to distinguish metasomatic processes related to volatile-rich fluids or to silicate melts (Aulbach et al., 2004). In our dataset, high $[\text{Sc}]_{\text{grrt}}$ is associated with high $(\text{Ce/Yb})_N$, indicating that volatile-rich metasomatism positively affects $[\text{Sc}]_{\text{grrt}}$ (Fig. 9b).
On the contrary, no correlation is visible between $[\text{Sc}]_{\text{grt}}$ and $(\text{Zr}/\text{Sm})_N$, confirming that metasomatism by silicate melts has a limited influence on $[\text{Sc}]_{\text{grt}}$.

### 3.5. Evolution of Scandium Concentration During Melting

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

### 4. Discussion

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

At the depths considered in the dataset, between 70 km and 200 km, garnet is the main host for Sc. It accounts for ca 75% of the Sc budget of the deep lithospheric mantle (Fig. 2a, regression curve), in agreement with the proportion of Sc incorporated in various lithotypes of mantle-rocks (Fig. 1b). Considering the median $[\text{Sc}]_{\text{grt}}$ from mafic and ultramafic rocks and estimates of the modal content of garnet (Perrillat et al., 2006; Stixrude and Lithgow-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 [Sc]_{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: \( D_{\text{Sc}}^{\text{grt}/\text{melt}} = 8.3 \) for eclogitic garnet and \( D_{\text{Sc}}^{\text{grt}/\text{melt}} = 6.0 \) 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 \( D_{\text{Sc}}^{\text{grt}/\text{melt}} \) on pressure, temperature and composition have been calibrated to experiments for the X site of garnet (van
Westrenen and Draper, 2007). However, the incorporation of Sc in mantle-derived garnets is not correlated with pressure or temperature (Figs. 5a, b and c), indicating the predominance of compositional effects.

4.4. Impact of Melt Extraction

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

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

4.5. Impact of Garnet Crystal Chemistry

Correlations between Sc and major elements (Fig 6) indicate the affinity of Sc for the uvarovite end-member of garnet ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$), indicating the significance of Cr in the crystal chemistry of mantle garnet. Although often referred to as a minor element, it can hardly be considered as such when it commonly reaches 0.5 apfu. In Cr-rich systems, the crystal-chemical mechanisms of Sc incorporation are unknown and $D_{\text{SC}}^{\text{grt/melt}}$ has not been determined.
experimentally, but experimental studies on garnet crystal-chemistry provide likely explanations on the influence of Cr. When the uvarovite component is limited, the composition is close to pyrope and Sc is mainly incorporated in the X site of garnet (Oberti et al., 2006). When the composition shifts toward the grossular end-member, with Cr content remaining low, the relaxation of the garnet structure by substitution of Mg$^{2+}$ ($r(^{VIII} \text{Mg}^{2+}) = 0.89 \, \text{Å}$, Shannon, 1976) for the larger cation Ca$^{2+}$ ($r(^{VIII} \text{Ca}^{2+}) = 1.12 \, \text{Å}$) results in an enlargement of both X and Y sites (Oberti et al., 2006; Kim et al., 2007) and increases the incorporation of Sc in these sites. However, in grossular, the size of the Y octahedron is constrained by the sole presence of the small Al$^{3+}$ cation ($r(^{VI} \text{Al}^{3+}) = 0.54 \, \text{Å}$), limiting the incorporation of Sc in the Y site (Oberti et al., 2006). When Sc substitutes for the larger Fe$^{3+}$ ion in the high-spin state (Lin and Wheat, 2012, $r(^{VI} \text{Fe}^{3+}, \text{high spin}) = 0.65 \, \text{Å}$) along the join andradite–eringaite, this barrier is removed, and Sc is incorporated exclusively in the Y site (Quartieri et al., 2006). Iron(III) has an ionic radius of similar to Cr$^{3+}$ ($r(^{VI} \text{Cr}^{3+}) = 0.62 \, \text{Å}$). By analogy, when the uvarovite component is significant, the less compact structure of Cr-Ca-rich garnet thus will favour the incorporation of Sc in the Y site. Large Y octahedra occupied by Cr and locally related to X dodecahedra occupied by Ca should coexist with small Y octahedra occupied by Al close to X dodecahedra occupied by Mg. Because Ca can reach 1.5 apfu, the result should be a highly strained structure. In these compositions, Sc might predominantly enter a highly deformed Y site close to X sites occupied by Mg, helping to reduce the strain because this X site is large compared to the one in pyrope.
This incorporation of Sc in the Y site of Ca-Cr-rich garnet is consistent with lattice-strain theory (Wood and Blundy, 2014), which relates the charge and radius of an ion to its partition coefficient in the crystallographic site of a given mineral species at a given temperature and pressure. From this theory and the experimental determination of trace-element partition coefficients, Onuma diagrams (Onuma et al., 1968) have been retrieved (Fig. 11) for mantle-related garnet end-members at thermobarometric conditions representative of the mantle (Corgne and Wood, 2004; Dasgupta et al., 2009; Corgne et al., 2012). Scandium is less compatible in the X or Y sites of the pyrope end-member than in the grossular end-member (Fig. 11a). The Onuma diagram expected from the interpretation given above is presented for the Y site for the uvarovite end-member as experimental data are not available. As explained above, incorporation of Cr and Ca in the garnet structure expands the Y site, increasing the compatibility of Sc in this site (Fig. 11b). This has a prominent effect on the variability of [Sc]_{grt}. As Sc compatibility in the Y site is low in pyrope, even a small expansion of the Y site can dramatically increase Sc compatibility.

This interpretation is consistent with the relationships between [Sc]_{grt} and [REE]_{grt}. Scandium is positively correlated with LREE and negatively with HREE (Fig. 8). The small ionic radius of Sc should make it more comparable to a HREE in terms of compatibility in the X site of garnet (Fig. 11a). However, the decrease in [Sc]_{grt} with increasing [HREE]_{grt} indicates that the compatibility of Sc in garnet falls as the compatibility of HREE increases. This can only be explained by the incorporation of part of the Sc in the Y site.
of garnet, while other HREE remain incompatible in the Y site of Cr-Ca-rich garnets (Fig. 11b). The shift towards the incorporation of Sc in the Y site of garnet tracks an enlargement of the X site of garnet, increasing the compatibility of LREE and explaining the positive correlation with Sc, while the effect on the compatibility of HREE remains limited. The incorporation of Sc in the Y site may also explain the poor correlation between $[\text{Sc}]_{\text{grt}}$ and the temperature and pressure of equilibration of garnet; a complex relationship depending on both X and Y sites could blur any existing trend.

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

4.6. Impact of Metasomatic Processes

Metasomatism of previously depleted rocks by silicate melts is not associated with variations in $[\text{Sc}]_{\text{grt}}$ (Fig. 9a). According to our melting model, Sc is mildly compatible in garnet-bearing mantle rocks. The Sc content of silicate melts is close from that of a garnet peridotite and $[\text{Sc}]_{\text{grt}}$ is not influenced by silicate-melt metasomatism. However, depleted garnets can reach high $[\text{Sc}]_{\text{grt}}$. A slight decrease in $[\text{Sc}]_{\text{grt}}$ exists along the silicate-melt metasomatism trend (from bright red to dark purple spots, Fig. 9a). In that case, the difference in Sc concentration between the garnet and the metasomatic
melt is great enough to lead to a decrease in $[\text{Sc}]_{\text{grt}}$.

Metasomatism by volatile-rich fluids is correlated with higher $[\text{Sc}]_{\text{grt}}$ (Fig. 9b), contrasting with the low mobility expected for Sc in fluids from the shallow lithospheric mantle (Lee et al., 2005). This behaviour is expected for strongly-incompatible elements (McKenzie, 1989; Bedini et al., 1997) but Sc is compatible in the garnet stability field of the mantle. Two mechanisms could explain the influence of volatile-rich fluids on $[\text{Sc}]_{\text{grt}}$. (i) At mantle pressures and temperatures, complexing of Sc by volatile elements transports significant amounts of Sc and drastically decreases its compatibility. This hypothesis is consistent with the occurrence of several Sc-rich carbonatites (up to 190 ppm Sc in whole-rock analyses, see e.g. Gramaccioli et al., 2000). However, few data are available on Sc-complexes in fluids except for hydrothermal fluids (Wood and Samson, 2006). Experiments indicate that $D_{\text{grt/fluid}}^{\text{Sc}}$ increases from silicate to carbonate-rich melts (Fig. 11a, Dasgupta et al., 2009). In the presence of garnet, carbonate-rich melts should not transport significant amounts of Sc compared to other melts. (ii) The second mechanism relies on the differences of compatibility between fertile and depleted garnet, which is not modified during metasomatism by volatile-rich fluids, as the fluids produced involve low volumes of melting (< 1 %, McKenzie, 1989). Volatile-rich fluids may be generated at the base of the lithosphere (McKenzie, 1989; Bedini et al., 1997). In this context, the deeper lithosphere is more fertile than in the upper parts, and consequently is richer in Sc (Fig. 10). Scandium is also mildly compatible due to the lower $D_{\text{Sc}}^{\text{grt/melt}}$ of fertile garnets compared to depleted ones. In this way, volatile-rich fluids can
be enriched in Sc compared to a depleted mantle. When these fluids ascend in the lithosphere and reach depleted parts of the mantle, the high compatibility of Sc in depleted garnets and the relatively high Sc concentration of the fluid combine to increase \([\text{Sc}]_{\text{g}}\).

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

**Impact of crystal chemistry.** Metasomatic events during the evolution of the subcontinental lithospheric mantle beneath the Siberian craton were inferred from peridotite xenoliths by Howarth et al. (2014). On the basis of the trends observed in the CaO–CrO\(_2\) diagram, increasing \([\text{Ca}]_{\text{g}}\) at constant \([\text{Cr}]_{\text{g}}\) is associated with a metasomatic refertilisation of harzburgite to lherzolite (Fig. 12a, arrow 1). Comparison with \([\text{Sc}]_{\text{g}}\) shows that harzburgitic garnets have high \([\text{Sc}]_{\text{g}}\) and refertilisation is associated with increasing \([\text{Sc}]_{\text{g}}\). Increased \([\text{Ca}]_{\text{g}}\) at constant \([\text{Cr}]_{\text{g}}\) increases Sc compatibility in garnet explaining the increased \([\text{Sc}]_{\text{g}}\) during this first stage of metasomatism.

The second stage is attributed to metasomatism by a kimberlitic melt, a product of small-degree partial melting (Fig. 12a, arrow 2). This event is associated with a decrease of \([\text{Sc}]_{\text{g}}\), from ca 150 ppm to ca 100 ppm, typical of lherzolitic garnet, and a decrease in \([\text{Ca}]_{\text{g}}\) and \([\text{Cr}]_{\text{g}}\), decreasing Sc compatibility in garnet. The third stage of metasomatism is associated with the percolation of extensive amounts of basaltic fluids (Fig. 12a, arrow 3). It is also associated with the strongest decrease of \([\text{Sc}]_{\text{g}}\), from ca 150 ppm to ca 50 ppm. This metasomatic event led to complete re-equilibration of garnet and increased modal garnet content, explaining the decrease in \([\text{Sc}]_{\text{g}}\).

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

**Impact of metasomatism.** Metasomatic events were proposed in the lithospheric mantle beneath the Canadian Shield, based on the geochemistry of xenoliths and xenocrysts from the Buffalo Hills kimberlite (Aulbach et al., 2004). The enrichment of incompatible elements in garnet and clinopyroxene was used to argue for an early stage of volatile-rich fluid metasomatism. In the Y–Zr diagram (Fig. 12c), most samples show high [Sc]$_{\text{grt}}$, between
ca 150 ppm and ca 250 ppm, regardless of the degree of depletion in terms of major elements. Volatile-rich metasomatism increases \([\text{Sc}]_{\text{grt}}\), explaining the disconnect between the degree of depletion and \([\text{Sc}]_{\text{grt}}\). The Y-Zr diagram also suggests the effects of silicate-melt metasomatism. Samples affected by this type of metasomatism exhibit a decrease in \([\text{Sc}]_{\text{grt}}\) (blue spots, Fig. 12c). This confirms that, when garnets are originally Sc-rich, silicate melt metasomatism can be seen in variations of \([\text{Sc}]_{\text{grt}}\).

Metasomatic processes were investigated in the lithospheric mantle beneath the Siberian craton (Agashev et al., 2013). The difference between the concentration of incompatible elements calculated from modal mineralogy and those measured was interpreted as reflecting the presence of cryptic phases induced by volatile-rich fluids during the formation of the garnet-bearing xenoliths. In the \((\text{Zr}/\text{Sm})_N-(\text{Ce}/\text{Yb})_N\) diagram (Fig. 12d), we observe an increase in \([\text{Sc}]_{\text{grt}}\) associated with increasing \((\text{Ce}/\text{Yb})_N\) at low \((\text{Zr}/\text{Sm})_N\). This trend is compatible with the influence of volatile-rich metasomatism on \([\text{Sc}]_{\text{grt}}\), showing that the signature of this metasomatic stage is preserved by \([\text{Sc}]_{\text{grt}}\) despite later stages of silicate metasomatism and Fe-rich metasomatism described by Agashev et al. (2013).

5. Conclusions

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

1. Garnet accounts for about 75% of the Sc budget of the deep lithospheric mantle, regardless of the context, thus controlling the mobility of Sc in the mantle.

2. High modal garnet contents in mafic rocks lead to dilution [Sc]_{grt}, leading to a specific geochemical behaviour of Sc in such host-rocks.

3. Melt extraction increases [Sc]_{grt} showing the compatibility of this element in the presence of garnet.

4. Crystal chemistry is the major parameter controlling [Sc]_{grt}. In particular, higher Cr# and Ca# in garnet increase the compatibility of Sc in this phase.

5. Metasomatism has limited effect on [Sc]_{grt} except in the specific case of volatile-rich fluids, which can greatly enhance [Sc]_{grt}.

These conclusions and the selection of case studies show how Sc geochemistry can help recognise fluid-related processes in the mantle. Scandium is mildly incompatible above the spinel–garnet transition zone (Mallmann and O’Neill, 2009) while this study shows that Sc behaves as a mildly compatible element in the garnet stability field. This unique behaviour results from the ability of this element to enter both X and Y sites of Cr-Ca-rich garnets, at the boundary between trivalent transition elements, which enter the Y site, and REE, which occupy the X site. This behaviour reflects the singular crystal chemistry of garnet from the lithospheric mantle, and emphasises the need for experimental studies on partitioning of trace elements in Cr-Ca-rich garnets. The balance between the variable compatibility of Sc in garnet,
depending on Cr# and Ca# and the modal garnet content of the host-rock induces subtle variations in compatibility which can have drastic effects on Sc contents, as shown by the unexpected effect of volatile-rich fluids on \([\text{Sc}]_{\text{grt}}\). In well-constrained contexts, studying Sc concentration will help to understand the conditions of generation of magmas, as well as the nature of their residues.

**Declaration of Interest**

None.

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Figure 1: Distribution of Sc concentration in minerals and mantle-related rocks: (a) box-and-whisker plots of Sc concentration in selected mantle-related rocks. The grey horizontal line corresponds to 16.4 ppm, the average Sc concentration in the silicate Earth (Palme et al., 2014); (b) box-and-whisker plots of Sc concentration in major rock-forming minerals. The box is limited by the first and third quartiles of the data distribution. The horizontal line represents the median, and the width of the adjacent notches shows the 95% confidence interval about the median. Where absent, this interval is narrower than the thickness of the line representing the median. The “whiskers” represent the last value before 1.5 times midrange (the arithmetic mean of maximum and minimum values) beyond the first or third quartile.
Figure 2: Influence of host-rock parameters on \([\text{Sc}]_{\text{grt}}\): (a) scatter plot of Sc concentration in the host-rock versus the estimated Sc content in the host-rock attributable to garnet. This estimate is calculated using the \([\text{Sc}]_{\text{grt}}\) and the modal content of garnet in the host-rock; (b) average proportion of Sc incorporated in the different mineral phases of garnet-bearing lherzolites, harzburgites, pyroxenites and eclogites (n: number of individual rocks analysed; after the only studies of the database reporting the required information: van Achterbergh et al., 2001; Grégoire et al., 2003; Ionov, 2004; Schmickler et al., 2004; Jacob et al., 2005; Ulianov et al., 2006; Appleyard et al., 2007; Gibson et al., 2008; Aulbach and Viljoen, 2015). Values of Sc concentration are sometimes absent for olivine and orthopyroxene grains, they are replaced by the median value calculated from the other studies reporting this content.

Figure 3: Density plot of \([\text{Sc}]_{\text{grt}}\) and histograms of \([\text{Sc}]_{\text{grt}}\) from mafic host-rock, fertile ultramafic host-rocks and depleted ultramafic host-rocks.
Figure 4: Variations in the distribution of $[\text{Sc}]_{\text{grt}}$ with the lithology of the host-rock: (a) box-and-whisker plots of $[\text{Sc}]_{\text{grt}}$ relative to the lithotype of the host-rock described in the original publications; (b) box-and-whisker plots of $[\text{Sc}]_{\text{grt}}$ in xenocrysts classified according to Grütter et al. (2004) (Xen.: all xenocryst values, G0: unclassified, G1: low-Cr megacrysts, G3: eclogitic, G5: pyroxenitic, G9: lherzolitic, G10: harzburgitic, G11: Ti-metasomatised, G12: wehrlitic). The box is limited by the first and third quartiles of the data distribution. The horizontal line represents the median, and the width of the adjacent notches shows the 95% confidence interval about the median. Where absent, this interval is narrower than the thickness of the line representing the median. The “whiskers” represent the last value before 1.5 times midrange (the arithmetic mean of maximum and minimum values) beyond the first or third quartile.

Figure 5: Influence of temperature and pressure on $[\text{Sc}]_{\text{grt}}$: (a) scatter plot of $T_{\text{Ni}}$ (Ryan et al., 1996) versus $[\text{Sc}]_{\text{grt}}$; (b) scatter plot of $T_{\text{BKN}}$ (Brey and Köhler, 1990) versus $[\text{Sc}]_{\text{grt}}$; (c) scatter plot of $P_{\text{BKN}}$ (Brey and Köhler, 1990) versus $[\text{Sc}]_{\text{grt}}$. Estimates of $T_{\text{BKN}}$ and $P_{\text{BKN}}$ are from the original publications.
Figure 6: Correlation matrix and scatter plots for $[\text{Sc}]_{\text{grt}}$ versus major and minor elements. Positive (respectively negative) correlations are indicated by red (respectively blue) colours and the orientation of the ellipse. The intensity of the correlation is given by the intensity of the colour (see colour bar) and the narrowness of the ellipse.

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

Figure 8: Correlation matrix and scatter plots for $[\text{Sc}]_{\text{grt}}$ versus REE. Positive (respectively negative) correlations are indicated by red (respectively blue) colour and the direction of the ellipse. The intensity of the correlation is given by the intensity of the colour (see colour bar) and the narrowness of the ellipse.
Figure 9: Scatter plots of Sc relationships to trace-element indicators of fluid-related processes in the mantle: (a) $[Y]_{\text{grt}}$ versus $[Zr]_{\text{grt}}$, the fields are after Griffin et al. (1999b); (b) $(\text{Ce/Yb})_N$ versus $(\text{Zr/Sm})_N$, ratios have been normalised to the values of McDonough and Sun (1995). The metasomatic trends are after Aulbach et al. (2004). The colour of each point depends on the Sc content of the record, from 0 ppm (in blue) to 300 ppm (in red).

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

Figure 11: Onuma diagrams (Onuma et al., 1968) showing the partition coefficients of trace elements as a function of their ionic radius: (a) X site of garnet (Prp: pyrope, Grs: grossular); (b) Y site of garnet (Maj: majoritic pyrope, Uv: uvarovite). Diagrams for the X site after van Westrenen and Draper (2007) and Dasgupta et al. (2009); diagram for the Y site of majoritic pyrope is from Corgne and Wood (2004) and an expected curve for the Y site of uvarovite is given to illustrate the influence of Cr and Ca incorporation.
Figure 12: Evolution of [Sc]$_{grt}$ with garnet composition in selected case studies: (a) evolution of [Sc]$_{grt}$ (given by the colour of each point) in the CaO–Cr$_2$O$_3$ diagram for garnets from the subcontinental lithospheric mantle beneath the Siberian craton (Hz: harzburgitic garnet, Lz: lherzolitic garnet). The arrows represent three stages of metasomatism, described by Howarth et al. (2014); (b) distinction of garnet groups from the Kaapvaal craton depending on their relative Sc contents and Cr/Ca ratios; data are from Gibson et al. (2008); (c) evolution of [Sc]$_{grt}$ (given by the colour of each point) in the Y–Zr diagram for garnets from the Buffalo Head Terrane (Dep.: depleted); data are Aulbach et al. (2004), and the fields are from Griffin et al. (1999b); (d) evolution of [Sc]$_{grt}$ (given by the colour of each point) in the (Zr/Sm)$_N$–(Ce/Yb)$_N$ diagram for garnets from the Siberian craton, data from Agashev et al. (2013). The metasomatic trends are after Aulbach et al. (2004).
Table Caption

Table 1: Comparisons of Sc concentration in the mantle calculated from this study with estimates from the literature for different mantle compositions. The references used for each value are given in the table. The estimated Sc 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 concentration of Sc in the type of garnet considered and 0.75 our assessment of the proportion of the Sc content in the mantle that is incorporated in garnet.