

Classifying crust- and mantle-derived garnet from a structural-chemical perspective

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Introduction

Garnets are arguably the most important indicator mineral and chemical-based classification diagrams are robust for diamond exploration. Some industry-accepted discriminants emphasize the importance of compositional variations such as Ca and Cr in peridotitic garnets (Grütter et al., 2004). However, chemical analysis elucidates only half of the story. Crystallographic information completes the story. In garnet (general formula $X_3Y_2Si_3O_{12}$), the divalent X cations enter an 8-coordinated triangular dodecahedral site and the trivalent Y cations enter the 6-coordinated octahedral site (Novak and Gibbs 1971). Chemical substitution in either or both sites controls the size of the garnet unit cell. Garnet is isometric with only one variable parameter, unit cell parameter a . This single parameter can be surprisingly informative. This work investigates the structural-chemical correlations for a suite of natural garnets using micro X-ray diffraction (μ XRD) and electron probe microanalysis (EPMA). These fundamental correlations, in turn, were used to establish new trends and to explore μ XRD as a reconnaissance tool in diamond exploration.

Methodology

A wide range of garnets were obtained from kimberlitic ($n=21$) and non-kimberlitic ($n=27$) sources worldwide. Samples were provided by various academic and industrial contacts. The majority of mantle-derived samples were selected to be representative of diamondiferous or potentially diamondiferous kimberlites from North American, African and Siberian Cratons. A collection of samples (drill cores, slabs, grain mounts and polished sections) was designated for detailed structural-chemical studies. Micro X-ray diffraction was performed using a Bruker D8 Discover X-ray diffractometer with $CoK\alpha$ radiation, Göbel mirror parallel beam optics and 300 μ m nominal beam diameter. EPMA was collected using a JEOL JAX-8530F electron microprobe, or the data was supplied by the sample provider. Unit cell parameters were refined based on non-linear least-squares refinement using the UnitCell software (Holland and Redfern, 1997). The crystallographic and compositional data for approximately 1400 garnet samples were compiled from previous and present studies, existing literature data, as well as the IMA database (truff.info/ima).

Results and Discussion

Within the suite of mantle-derived garnets, peridotitic garnets range from pale mauve to purple in color, whereas eclogitic garnets are orange. Wehrlitic green garnets were occasionally observed in a few localities (e.g., Mud Lake kimberlite field, Sandeman et al., 2007). Garnet populations across the world's kimberlites demonstrate appreciable variations in their Ca and Cr contents (Fig. 1). Lherzolitic (G9) and harzburgitic (G10) garnets cover a great range of chromium content (1.02-14.28 wt.% Cr_2O_3). Crustal garnets are enriched in almandine \pm andradite and normally contain higher Ca and Fe contents than mantle-derived garnets. The larger ionic radii of Ca (1.12 Å) and Fe^{2+} (0.92 Å) compared to Mg (0.89 Å), accompanied by the larger size of Fe^{3+} (0.645 Å) relative to Al (0.535 Å) and Cr (0.615 Å), will enlarge the unit cell size when substitution occurs. Other radii of relevance are Mn (0.93 Å), Ti (0.605 Å), Zr (0.72 Å), V (0.64 Å).

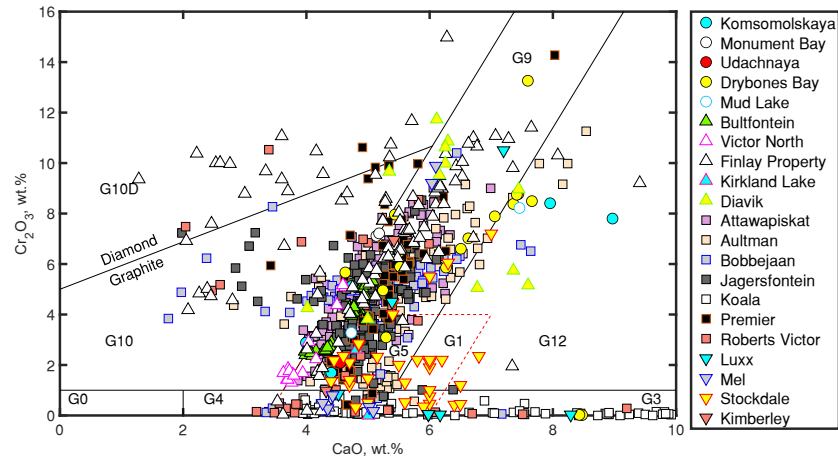


Figure 1: Compositional variations in garnet plotted as a Cr_2O_3 versus CaO classification diagram (Grütter et al., 2004). Stockdale and Kimberley garnet data are from Rost et al. (1975) and Antao (2021), respectively. Attawapiskat, Aultman, Bobbejaan, Jagersfontein, Koala, Premier, and Roberts Victor garnet data are from Harwood (2009). Other samples are from this study.

The peridotitic G9 and G10 garnets show pronounced structural-chemical trends that are predominantly controlled by Al-Cr substitution in the octahedral site (Fig. 2 a and b) with some Mg-Ca substitution in the triangular dodecahedral site (Flemming, 2007; Harwood, 2009). The unit cell parameters of eclogitic G3 and pyroxenitic G4 garnets correlate positively with Ca. However, G3 garnets extend to larger unit cells due to their higher amounts of Ca. Data for the G3 garnets are scattered because of a variety of Y-site substitutions (Fig. 2c). Wehrlitic G12 garnets can be easily distinguished from pyroxenitic G4 and harzburgitic G10 garnets based on their larger unit cell size, resulting from the higher content of Cr and Ca (Fig. 2b and c). The G10 garnets have a smaller unit cell size than eclogitic garnets because of the high amount of Mg in the X site.

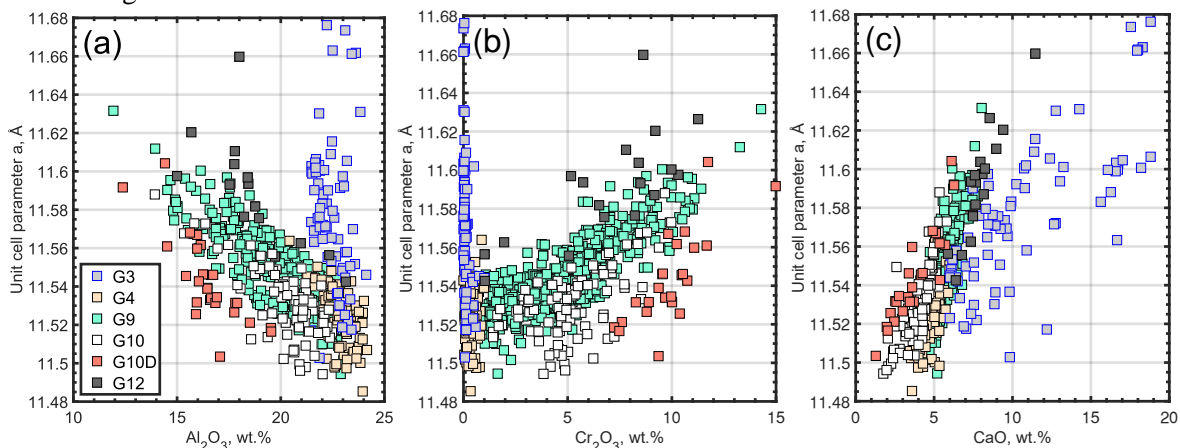


Figure 2: Unit cell parameters determined for garnet, expressed as a function of chemical composition. (a) Unit cell versus Al_2O_3 ; (b) Unit cell versus Cr_2O_3 and (c) Unit cell versus CaO . Garnets from various localities have been grouped together based on their Grütter et al. (2004) classification to create an overall plot for each mantle garnet type.

Our results suggest that peridotitic Cr-pyrope garnets (G9, G10 and G12) are characterized by small unit cell parameters (11.494-11.660 Å), whereas more dramatic changes were observed for eclogitic almandine garnets (G3; 11.503-11.858 Å). Garnets derived from upper crust (e.g., grossular-andradite-uvarovite) plot toward high unit cell values, forming a broad field between 11.837 Å and 12.122 Å (Fig. 3a). Unit cell sizes of Ti-rich and kimzeyite garnets are noticeably expanded (>12.061 Å) due to large radii of octahedral occupants Ti and Zr, respectively.

are shown along the major cation substitutions between end members (Fig. 3b). Therefore, unit cell parameter derived from μ XRD may serve as a reconnaissance tool for identifying garnets for further chemical analysis; garnets with unit cell parameter less than 11.660 Å are potentially peridotitic, whereas garnets with unit cell parameter larger than 11.660 Å are not peridotitic. Harzburgitic G10 garnets have unit cell parameter below 11.604 Å.

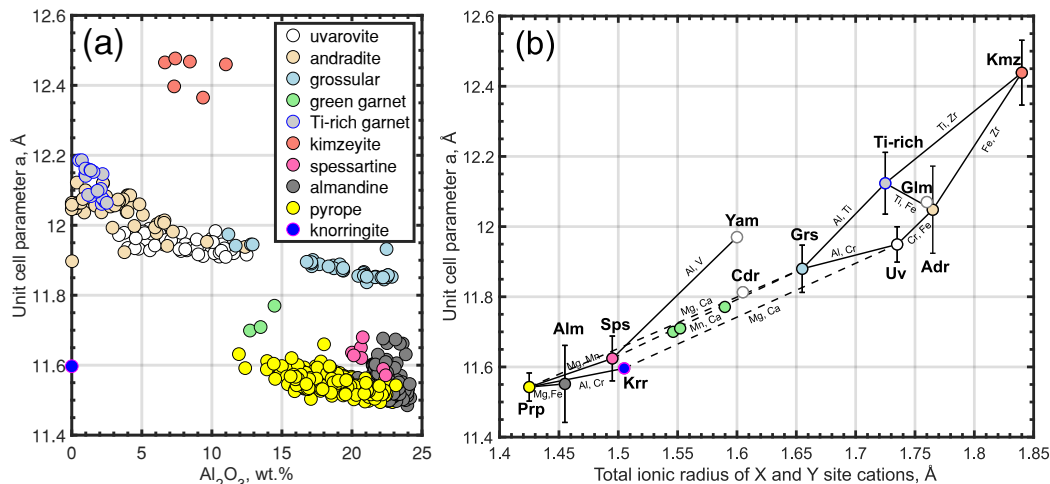


Figure 3: Plots of garnet unit cell parameter versus (a) Al_2O_3 and (b) sum of the ideal ionic radii of the cations occupying the triangular dodecahedral (X) and octahedral (Y) sites (Shannon, 1976). Connected solid lines denote cation exchange between end members. Dashed lines indicate a miscibility gap. Circles are the averages of unit cell parameter with error bars representing 2 standard deviation uncertainties. End-member knorringite (Krr; $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$), calderite (Cdr; $\text{Mn}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}$), goldmanite (Glm; $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$), yamatoite (Yam; $\text{Mn}_3\text{V}_2\text{Si}_3\text{O}_{12}$) unit cell data are taken from Klein and Dutrow (2008), whereas the rest are from the compiled data in this work. Prp = pyrope (mainly Cr-pyrope), Alm = almandine, Sps = spessartine, Grs = grossular, Ti-rich = Ti-rich garnet (scholormite and morimotoite), ADR = andradite, Uv = uvarovite, Kmz = kimzeyite ($\text{Ca}_3\text{Zr}_2(\text{SiAl}_2)\text{O}_{12}$).

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