# LETTER

# Magnesium K-edge EXAFS study of bond-length behavior in synthetic pyrope-grossular garnet solid solutions

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#### ABSTRACT

Direct structural characterization of the changes in the local environment of Mg occurring in the garnet structure as a function of the Ca content are determined by Mg *K*-edge X-ray absorption fine structure on synthetic samples along the pyrope-grossular join. With increasing Ca content, the short Mg-O2 distance of the dodecahedron slightly decreases, while the long Mg-O4 distance tends to increase, so that the dodecahedron is more distorted in grossular-rich garnets than in end-member pyrope. This quantitative direct description of the changes in the local environment of Mg in the pyrope-grossular solid solution confirms and better defines previous experimental and recent computational results.

Keywords: Pyrope-grossular garnets, EXAFS, magnesium, local environment

#### INTRODUCTION

Most rock-forming silicates are solid-solution phases. Studies of their crystal-chemical properties are mandatory to understand, for example, the role of structural heterogeneity and micro/nano strain. It governs thermodynamic and physical behavior and also controls how minor and trace elements can be incorporated. The concept that the local coordination around a specific cation depends not only on its atomic radius, but also on bulk composition, is of importance (for garnets: Quartieri et al. 1995, 1999a, 1999b, 2002, 2004, 2006; Bosenick et al. 1999; Freeman et al. 2006; for amphiboles: Oberti et al. 2007). This issue is necessary for instance, for modeling and interpreting trace-element partitioning behavior and various petrogenetic studies (van Westrenen et al. 1999, 2003). Among the rock-forming silicates, garnets (X<sub>3</sub>Y<sub>2</sub>Z<sub>3</sub>O<sub>12</sub>) are stable over a wide range of temperature and pressure, and are abundant in Earth's crust, upper mantle, and transition zone. The aluminosilicate garnet structure has the space group  $Ia\overline{3}d$ , where all the cations are located in special crystallographic positions. The site symmetries are 222 for X,  $\overline{3}$ for Y, and 4 for Z, while the oxygen atom is located in a general position. The garnet structure consists of a corner-sharing threedimensional network of SiO<sub>4</sub> tetrahedra and AlO<sub>6</sub> octahedra, where the triangular-dodecahedral cavities host the divalent Xcations. An important feature of the garnet structure is the high number of edges shared by each X dodecahedron with adjacent tetrahedra (2), octahedra (4) and dodecahedra (4). Thus, changes

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coordination polyhedra in the crystal structure. The thermodynamic mixing behavior of pyrope (prp,

in the geometry of the dodecahedron affect the geometry of all

 $Mg_3Al_2Si_3O_{12}$ -grossular (grs,  $Ca_3Al_2Si_3O_{12}$ ) garnets is important because it is highly non-ideal. This non-ideality has been shown in a number of different investigations (Newton et al. 1977; Ganguly et al. 1993; Bosenick et al. 2000, 2001; Vinograd et al. 2006; Dachs and Geiger 2006), and it is generally ascribed to the disparate size of the X cations in the solid solution (e.g.,  $^{[8]}Ca = 1.12$  Å,  $^{[8]}Mg = 0.89$ ), which causes elastic strain on a local scale (Dapiaggi et al. 2005).

From a structural point of view, nonlinearity in crystal-chemical properties can be observed both at the long-range scale as measured by diffraction measurements (Armbruster et al. 1992; Merli et al. 1995; Ungaretti et al. 1995) and at the short-range scale by spectroscopy (see Geiger 2004 for a review). A crucial topic of study concerns the relationships between non-linearity in the structural properties and non-ideality in the thermodynamic mixing behavior (Dapiaggi et al. 2005; Geiger 2007).

We have recently studied the local structural environments around Ca and Sc in synthetic (Sc-doped) prp-grs garnets by X-ray absorption spectroscopy at the Ca and Sc *K*-edge, in both the extended (EXAFS) and near edge (XANES) regions (Oberti et al. 2006a, 2006b). Analysis of the spectra, based on a model provided by X-ray structure refinements, showed that the longer Ca-O4 bond length shortens considerably with increasing pyrope content, whereas the Ca-O2 bond length increases slightly. The two bonds have similar values in grs-poor solid solutions (i.e., Ca-O2  $\approx$  Ca-O4  $\approx$  2.35  $\pm$  1 to 2.36  $\pm$  1 Å). The experimental

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evidence of significant shortening of the Ca-O4 bond length as a function of prp content is consistent with computational studies by Bosenick et al. (1999, 2001) and Freeman et al. (2006). A different behavior for Ca-O2 bond has been proposed, because the computational results indicate little variation of the short bond distance along the prp-grs join. To better understand the behavior of X-O bonding in prp-grs garnets, structural information on the local environment around Mg along the join is mandatory. In this letter, we cover this gap, reporting the results of a Mg K-edge XAFS study done on the same pyp-grs garnet samples used for the experiments at the Ca and Sc K-edges. Due to the experimental difficulties in studying light elements by EXAFS (see below), normally only the near edge region (XANES) of the absorption spectra has been used to study magnesium local environment. Few EXAFS studies are reported in the literature (Ildefonse et al. 1995; Jupe et al. 2001; Sankar et al. 2001). There are various difficulties in undertaking Mg K-edge XAFS measurements, which include:

(1) The limited number of facilities worldwide that provide a beam of sufficient brilliance and monochromaticity in the required energy range (Mg *K*-edge being around 1300 eV). This is near the high-energy limit for grating monochromators and the low energy limit for crystal monochromators.

(2) Even for samples with high Mg contents, transmission measurements are impossible or difficult, due to the high photoelectric absorption cross-sections. Thus, thin samples should also possess a high lateral homogeneity. Therefore, Mg-rich samples are measured in the fluorescence or electron-yield mode. This requires self-absorption effects to be taken into account.

(3) The range of photoelectron wavenumbers is often limited due to the closely spaced absorption edges in the soft X-ray range.

Therefore, the purpose of this study is twofold: first, we investigate further the nature of local relaxations occurring in garnets along the prp-grs join; second, we report the first EXAFS measurements made to describe the local environment around the Mg atom in a complex silicate matrix.

#### EXPERIMENTAL AND DATA ANALYSIS

Details of the synthesis conditions, chemical analysis, and X-ray diffraction (XRD) characterization of the Sc-doped garnets (prp, prp<sub>60</sub>grs<sub>40</sub>, prp<sub>20</sub>grs<sub>80</sub>) are reported in Oberti et al. (2006a, 2006b). For this work, samples were prepared by grinding the garnet powders in a mortar to reduce the grain size, and then deposition on a carbon tab. Magnesium *K*-edge XANES and EXAFS spectra were recorded at the BEAR beamline (Nannarone et al. 2004) of the ELETTRA synchrotron light source (Trieste, Italy), in the fluorescence yield mode using a HP-Ge solid state detector. MgO was used as a reference compound to test the reliability of data collection and analysis procedures.

The raw XANES spectra were subtracted from the pre-edge background and then normalized to 1 on the high-energy side (at 1360 eV) to allow comparison of samples with different absorber contents. Since Mg is not a dilute element in the samples, fluorescence yield spectra are not directly proportional to the absorption coefficient, due to self-absorption effects; hence, the spectra were corrected following the procedure outlined in Carboni et al. (2005).

The EXAFS absorption spectra were collected in the energy range 1210–1560 eV; the upper limit is forced by the Al *K*-edge at 1559 eV. Structural EXAFS signal  $\chi(k)$  has been calculated using a standard extraction procedure: pre-edge subtraction, energy scale definition (E<sub>o</sub>) and post-edge absorption calculation ( $\mu_o$ ), parameters which first were tailored to the MgO reference sample. The post-edge atomic absorption background ( $\mu_o$ ) was calculated by fitting a polynomial spline to the data in the energy range 1321–1535 eV. Spectra were analyzed in the k range 2–7 Å<sup>-1</sup> by least-squares fitting directly the raw k $\chi(k)$  data; we found this choice more

reliable than the conventional Fourier filtering approach, as the Fourier transform in the limited available spectral range was found to produce quite large distortions. Theoretical amplitude and phase shift functions were calculated by FEFF8.0 (Ankudinov et al. 1998) assuming the crystallographic structure of Sc-doped pyrope (Oberti et al. 2006a). All the two-body signals (single-scattering contributions) derived from the crystallographic models out to about ~4 Å were considered; multiple scattering contributions were found to be of negligible amplitude. The multiplicity of each signal was fixed to its crystallographic value. An error analysis was performed using the capabilities of MINUIT (James 1994) to determine the confidence limits on the refined parameters and the covariance matrix. Previous XAFS investigations performed on these garnets at the Sc K-edge (Oberti et al. 2006b) revealed the incorporation of about 0.3 apfu of Sc in the X dodecahedral site of pyrope, with the consequent local charge balance obtained by substitution of some Mg in the adjacent Z tetrahedron (about 0.15 apfu). Similar amounts of Sc were incorporated in the solid solutions, but distributed over different crystallographic sites. The limited wavenumber range of our data did not allow inclusion in the fits of the minor amounts of Sc and Mg. Hence, EXAFS data for the Sc-doped pyrope were fitted with seven contributions (Table 1): the first two are single scattering ones due to eight oxygen ion nearest neighbors (four O1 and four O2), two Si atoms in tetrahedral coordination, four Al atoms in octahedral coordination, four Si atoms and four Mg atoms at the same distance from the central absorbing atom, and an outer shell of oxygen atoms. In consideration of the limited wavenumber range, the fitting procedure was conducted as follows: first, photoelectron energy scale origin ( $E_0$ ), the bond distances ( $R_i$ ), and the Debye-Waller (DW) factors of the nearest oxygen atoms were refined, keeping the  $R_i$  values of the outer shells fixed to their crystallographic values; subsequently, the  $R_i$  values and the DWs of the outer shells were adjusted keeping fixed the nearest oxygen shells. Moreover, the same DW factor was used for the outer Si, Al, and Mg shells. This is an arbitrary choice but mandatory to avoid the correlations among DWs of outer shells. Notice that the imposed link on the DWs reduces the reliability on their absolute values, but strengthens the confidence on the observed interatomic distances. For the solid-solution samples prp60grs40 and prp20grs80, the Mg-Ca contribution (instead of Mg-Mg) was considered in the fitting procedure.

## **RESULTS AND DISCUSSION**

The measured XANES spectra are shown in Figure 1. The spectra, displayed from top to bottom as a function of the Mg concentration, are all similar. They are characterized by the presence of four peaks (A to D in Fig. 1) at the same energy positions. As discussed by Ildefonse et al. (1995), this indicates that the local structural environment around Mg is substantially maintained and that only minor variations in the overall geometry occurs around Mg. In contrast, more significant differences were observed by Oberti et al. (2006a) in the Ca *K*-edge XANES spectra for  $prp_{60}gr_{s40}$  and  $prp_{20}gr_{s80}$  solid solutions. The strong variations in the EXAFS signals were interpreted as showing significant variations in the local Ca environment along the prp-grs binary. The results of the Mg *K*-edge EXAFS data analysis are reported in Table 1, Figures 2 and 3. In particular, for a comparison, Figure 3 shows as a function of prp mole fraction the experimental Mg-O

 TABLE 1.
 Local structure around Mg in pyrope and garnet solid solutions as obtained by EXAFS fitting results

	Pyrope		prp <sub>60</sub> grs <sub>40</sub>		prp <sub>20</sub> grs <sub>80</sub>	
	R (Å)	DW (Ų)	R (Å)	DW (Å <sup>2</sup> )	R (Å)	DW (Ų)
Mg-O2 ×4	2.19 (4)	0.017(7)	2.18(2)	0.010(5)	2.17(3)	0.02(1)
Mg-04 ×4	2.32(6)	0.026(6)	2.37(3)	0.013(5)	2.38(5)	0.03(1)
Mg-Si ×2	3.12(2)	0.001	3.00(3)	0.007(2)	3.01(3)	0.008(2)
Mg-Al ×4	3.34(2)	0.001	3.28(3)	0.007(2)	3.29(3)	0.008(2)
Mg-Mg(Ca) ×4	3.48(2)	0.001	3.49(3)	0.007(2)	3.52(3)	0.008(2)
Mg-Si ×4	3.48(2)	0.001	3.49(3)	0.007(2)	3.52(3)	0.008(2)
Mg-O×8	4.24(2)	0.002	4.14(3)	0.013(2)	4.17(3)	0.016(2)

Notes: For Pyrope, k-range = 2.0-7.6,  $\Delta E_0 = 2.16$ ,  $R^2 = 0.25$ . For prp<sub>60</sub>grs<sub>40</sub>, k-range = 2.0-7.6,  $\Delta E_0 = 4$ ,  $R^2 = 0.18$ . For prp<sub>20</sub>grs<sub>30</sub>, k-range = 2.0-7.1,  $\Delta E_0 = 3.8$ ,  $R^2 = 0.23$ .  $R^2 = {\Sigma_k [k^{\infty} \chi^{eop}(k) - k^{\infty} \chi^{mod}(k)]^2}/{{\Sigma_k [k^{\infty} \chi^{eop}(k)]}} = normalized residual goodness function that is an indicator of overall fit quality, accordingly to the recommendations of the Standards and Criteria Committee of the International XAFS Society.$ 

bond distances determined in this work, those deduced by Geiger and Armbruster (1999) from an X-ray refinement on garnet of composition grs<sub>90</sub>prp<sub>10</sub>, and the values determined by Freeman et al. (2006) by ab-initio calculations along the prp-grs join. The final fit to the EXAFS pyrope signal (Fig. 2a) reproduces the main features of the experimental data. The raw, unfiltered experimental data are reported, since no Fourier filtering was used. The fit reproduces well the frequency components of the experimental spectrum up to the highest considered, as can also be appreciated from the residual reported in the same figure. Considering the limited k-range of the EXAFS data, the quality of this fit can be considered satisfactory and reinforces our confidence in the reliability of our experimental results. Moreover, the bond distances determined by the fit [i.e., 2.19(4) and 2.32(6) Å in Table 2] are in good agreement with those determined for pyrope by single-crystal XRD [2.205(1) and 2.345(1) Å, after Oberti et al. 2006a]. The fits for the solid-solution samples are reported in Figures 2b and 2c, and comments similar to the ones made above concerning the fit of the pyrope spectrum can be made. The EXAFS results indicate that with decreasing Mg content from prp to prp<sub>20</sub>grs<sub>80</sub>, the long Mg-O distance tends to increase in length, while the shorter bond remains roughly constant or slightly contracts in length. The inspection of the outer Mg-O shell (last line of Table 1) reveals that it undergoes a slight contraction with decreasing Mg content. Focusing on the first Mg-O shells, our results show that Mg-O2 and Mg-O4 bonds in grs-rich garnet differ in length from one another more than they do in the end-member pyrope. This Mg-O bond behavior is in good agreement with the computational results of Freeman et al. (2006), even if the longer Mg-O4 distance is larger than that determined by EXAFS analysis. The results are also in satisfactory agreement with the experimental data of Geiger and Armbruster (1999) for the garnet grs<sub>90</sub>prp<sub>10</sub>. This solid solution was studied by single-crystal XRD at 295 and 100 K, and they concluded that Mg tends to assume a "quasi fourfold" oxygen coordination (Mg-O2 = 2.1 Å, Mg-O4 = 2.5 Å), which is measurably different from the bond lengths in pyrope. The results of our work allow us to determine better, with a direct experimental approach, the effects of composition on local environments around the Mg atom in prp-grs garnets. Indeed, our EXAFS results obtained on the sample prp<sub>20</sub>grs<sub>80</sub> agree with the trend proposed by Geiger and



**FIGURE 1.** XANES spectra at the Mg *K*-edge. Individual spectra have been normalized with respect to the high-energy side of the curve. Labels A to D refer to the main features present in the spectra.

Armbruster (1999) for Mg-O bond distances, but indicate a less deformed Mg coordination geometry [i.e., Mg-O2 = 2.17(3) Å, Mg-O4 = 2.38(5) Å]. Finally, we can further test the reliability of our XAS results by comparing the mean X-O bond distances determined by single-crystal XRD on  $prp_{60}grs_{40}$  and  $prp_{20}grs_{80}$  garnets (Oberti et al. 2006a) with the values calculated by averaging the EXAFS bond lengths on the basis of their contribution to the mean value determined by XRD on the solid solution. The XRD-based mean values for the dodecahedral X-O distances are 2.320(1) and 2.382(1) Å for  $prp_{60}grs_{40}$  and  $prp_{20}grs_{80}$ , respectively. The corresponding mean distances determined by EXAFS data are 2.31 and 2.36 Å, respectively, in good agreement with the XRD values.

The results of this work have highlighted the effects of the Mg:Ca substitution in causing Mg-O bond-length variations



**FIGURE 2.** The k-space EXAFS fit results for end-member pyrope and  $prp_{60}grs_{40}$  and  $prp_{20}grs_{80}$  garnet solid solutions. Solid line = experimental data; dots = fitted signal; dashed line = residual. Also shown are the individual contributions to the EXAFS signal.



**FIGURE 3.** Variations in the experimental and computationally determined Mg-O bond lengths as a function of prp mole fraction in the solid solution. Full symbols = this work; open symbols = Freeman et al. 2006; crossed symbols = Geiger and Armbruster (1999).

along prp-grs join, and will contribute to understand—from a crystal-chemical perspective—the thermodynamic mixing behavior of prp-grs garnets. Moreover, the direct experimental demonstration that the local dodecahedral environment of Mg undergoes a significant deformation as a function of the grs content, will have also implications on the models used to interpret the partitioning behavior of minor and trace elements into this garnet solid solution.

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