## Cation order-disorder in Fe-bearing pyrope and grossular garnets: A <sup>27</sup>Al and <sup>29</sup>Si MAS NMR and <sup>57</sup>Fe Mössbauer spectroscopy study

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## ABSTRACT

A suite of Fe-bearing natural and synthetic grossular-rich [(Ca,Fe)<sub>3</sub>(Al,Fe)<sub>2</sub>Si<sub>3</sub>O<sub>1</sub>] and pyrope-rich [(Mg,Fe)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>] garnets were investigated using <sup>27</sup>Al and <sup>29</sup>Si MAS NMR and <sup>57</sup>Fe Mössbauer spectroscopy. This was done to study the state of cation order-disorder in garnet solid solutions by analyzing paramagnetically shifted resonances in high-resolution NMR spectra. The Mössbauer spectra, along with electron microprobe results, give the concentrations of  $Fe^{2+}$  and  $Fe^{3+}$  and their site occupancies, even in grossular samples with very low concentrations of Fe. MAS NMR spectra were collected on Fe<sup>2+</sup>-bearing grossular- and pyrope-rich garnets with up to 25 mol% almandine component and on other Fe<sup>3+</sup>-bearing grossular samples with up to 9 mol% andradite component. Despite peak broadening and signal loss, structural information was even obtained from garnet with relatively high Fe contents (25 mol% almandine component). Paramagnetically shifted NMR peaks, related to the presence of Fe<sup>2+</sup>, were observed in grossular samples and are similar in nature to those reported previously for natural, relatively low-Fe<sup>2+</sup> pyrope garnets by Stebbins and Kelsey (2009). Additional NMR peaks appear as the concentration of Fe<sup>2+</sup> increases, reflecting an increase in the average number of neighboring Fe<sup>2+</sup> cations around  $AlO_6$  and  $SiO_4$  groups. These newly observed peaks hold potential to provide information concerning the presence or absence of short-range ordering in certain Fe-bearing silicate garnets. The effect of Fe<sup>3+</sup> on the MAS NMR spectra of garnet appears to be less pronounced, because it does not produce any observable paramagnetically shifted resonances.

**Keywords:** NMR spectroscopy, Mössbauer spectroscopy, pyrope, grossular, almandine, garnet, paramagnetic shifts, short-range order