Scandium-45 NMR of pyrope-grossular garnets: Resolution of multiple scandium sites and comparison with X-ray diffraction and X-ray absorption spectroscopy

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ABSTRACT

Here we present 45Sc and 27Al NMR results on Sc-doped pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$), grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$), and an 80% grossular-20% pyrope garnet (grs80) that have recently been well-studied by X-ray diffraction and X-ray spectroscopies. Clearly distinct NMR peaks are observed for Sc in the eight-coordinated X site (pyrope and grs80) and in the six-coordinated Y site (grossular and grs80). X-ray and NMR data agree that only eight-coordinated Sc is present in pyrope and that six-coordinated Sc is predominant in grossular; however, the XRD results also indicated significant X and Z site (four-coordinated) Sc in the Ca-rich garnet. Possible reasons for this apparent discrepancy are discussed. We demonstrate that 45Sc NMR is potentially a useful new method for studies of the site occupancies of Sc$^{3+}$ in oxides and silicates, at least in experimental systems where its concentration is a few percent or greater.

Keywords: Crystal structure, pyrope-grossular garnet, scandium in garnet, NMR spectroscopy, pyrope-grossular garnet, scandium-45, aluminum-27

INTRODUCTION

Determination of the sites occupied by minor and trace elements in minerals is essential for physically accurate models of partitioning, solubility, diffusivity, and other properties. Among the experimental methods that are available to study local structure (as opposed to the long-range average structure obtainable by diffraction) around ions in relatively low concentrations in solid solutions, such as optical and X-ray spectroscopies, nuclear magnetic resonance (NMR) has only occasionally been used, largely because of its relatively low sensitivity. However, for relatively “favorable” nuclei, several studies have shown the ability of this technique to resolve and quantify local structural information (e.g., coordination number) for minor components in systems such as Li in beryl (Sherriff et al. 1991), B in calcite and aragonite (Sen et al. 1994), Al in MgSiO$_3$, perovskite, stishovite, and rutile (Stebbins et al. 2006; Stebbins 2007), Al in Ca-silicate cement minerals (Skibsted et al. 1994), and B, P, Cs, and Na sorbed onto mineral surfaces (Kim and Kirkpatrick 1997, 2004, 2006). High magnetic fields have often facilitated such studies, by enhancing sensitivity and reducing peak broadening for quadrupolar nuclides such as $^1$B, $^{23}$Na, and $^{27}$Al.

Scandium, although rare in nature, is an interesting trace element in silicate minerals because it occurs exclusively as a trivalent cation and has a radius between those of Al$^{3+}$ and the rare earths. It is also the lightest of the transition metals. The applications of Sc in technology are limited in part because of its high cost, but it has real interest for oxide ion conductors in fuel cells and other devices: doping with Sc$^{3+}$ gives the highest conductivity in the widely used family of zirconia-based ceramics (Kim et al. 2006). Sc$^{3+}$ can be a significant element in minerals, for example in a natural scandian garnet (Galuskina et al. 2005) and in synthetic solid solutions [e.g., Ca$_3$Fe$_2$Si$_3$O$_{12}$-Ca$_3$Sc$_2$Si$_3$O$_{12}$ (Quartieri et al. 2006) and Y$_3$Al$_2$Al$_3$O$_{12}$-Y$_3$Sc$_2$Al$_3$O$_{12}$ (Tien et al. 2002) garnets]. Experimental (van Westrenen et al. 1999), theoretical (van Westrenen et al. 2003; Freeman et al. 2005), and structural (Oberti et al. 2006) studies have been made of the partitioning and substitution mechanism of Sc$^{3+}$ (and of numerous other trace elements) in pyrope-grossular garnets.

$^{45}$Sc is, in principle, a quite favorable nuclide for solid-state NMR, having 100% natural abundance and a resonant (Larmor) frequency not far below the widely studied $^{27}$Al, both leading to high sensitivity. Its relatively large quadrupolar moment ($Q = -0.22 \times 10^{-28}$ m$^2$ vs. 0.14 $\times 10^{-28}$ m$^2$ for $^{27}$Al) can lead to broad NMR peaks, as can its larger range in chemical shift and hence sensitivity of peak position to minor local structural variations induced by disorder. However, its higher nuclear spin quantum number ($I = 7/2$ vs. 5/2 for $^{27}$Al) reduces quadrupolar broadening by more than a factor of two for the same values of the quadrupolar coupling constant ($C_Q$). Only a few high-resolution, solid-state $^{45}$Sc NMR studies have appeared, including a study of this nuclide in YAG (Y$_3$Al$_2$Al$_3$O$_{12}$-Y$_3$Sc$_2$Al$_3$O$_{12}$) solid solutions (Tien et al. 2002), in complex Sc-phosphates (Riou et al. 2002; Park et al. 2004), and early work on several Sc salts (Thompson and Oldfield 1987). Recently, data for several H- and F-free Sc-containing oxides were reported, which showed a rough correlation between Sc coordination number (either 6 or 8) and the isotropic chemical shift, allowing new inferences on the mean and range of Sc coordinations in Sc-doped ZrO$_2$ (Kim et al. 2006). In a detailed study of $^{45}$Sc in several compounds with organic and