^{27}Al and ^{29}Si MAS-NMR and ^{57}Fe Mössbauer study of iron-bearing grossular and pyrope garnet: Implications for order/disorder

AARON C. PALKE*[1], JONATHAN F. STEBBINS[1], CHARLES A. GEIGER[2] AND GEROLD TIPPELT[2]

[1]Department of Geological and Environmental Sciences, Stanford University
(apalke@stanford.edu, *presenting author)
[2]Department of Materials Science and Physics, Section Mineralogy, University of Salzburg

Many natural silicate garnets ($X_3Y_2Si_3O_{12}$) exist as solid solutions between the various end-members with mixing of different divalent and trivalent cations on the X site and Y sites, respectively. The rich crystal chemistry exhibited by the garnet group has been used to provide information on the petrogenesis of the geologic formations containing this mineral. Questions of long- and short-range order/disorder of cations on the X and Y sites bear importance in thermodynamic investigations of garnets and have been the subject of much research over the years.

We report here the results of an ^{57}Fe Mössbauer and ^{27}Al and ^{29}Si Magic-Angle Spinning Nuclear Magnetic Resonance study of a suite of natural and synthetic Fe-bearing grossular-rich ($Ca_3Al_2Si_3O_{12}$) and pyrope-rich ($Mg_3Al_2Si_3O_{12}$) garnets. Samples were characterized by electron probe microanalysis for their chemical compositions with relative amounts of Fe^{2+} and Fe^{3+} on the X and Y sites, respectively, measured by ^{57}Fe Mössbauer spectroscopy. The Fe content varies among the samples with up to 10 mol % of an almandine component ($Fe_3Al_2Si_3O_{12}$) in both pyrope- and grossular-rich garnets providing clearly interpretable and informative NMR spectra. Grossular-rich garnets have the additional complication of variable Fe oxidation state with both Fe^{2+} and Fe^{3+} present in most samples.

Fe^{2+} in these garnets produces distinct paramagnetically shifted NMR peaks. We assign these peaks to distinct local ^{27}Al-Fe^{2+} and ^{29}Si-Fe^{2+} configurations in the garnet crystal structure. The greater frequency shifts for these resonances, as compared to ordinary diamagnetic NMR chemical shifts allows, in many instances, for greater resolution between specific atomic configurations. The areas of these peaks can then be compared to predictions based on random or ordered distributions of Fe^{2+} in the garnet structure. This technique has the potential to provide information on short-range order/disorder of Fe^{2+}-bearing garnet and in other geologically important silicate systems.