

Paramagnetic interactions in solid-state Nuclear Magnetic Resonance: Short-range order in Fe-bearing geological materials

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Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) is a powerful spectroscopic tool for the elucidation of atomic structure of geological materials. Of particular interest to Earth Scientists are NMR-active nuclides ^{17}O , ^{27}Al , and ^{29}Si among others. The small length scale of NMR interactions coupled with the site-specific, generally quantitative nature of the NMR experiment makes MAS-NMR spectroscopy useful for addressing questions of short-range ordering and trace- to minor-element substitution in geologically important minerals. MAS-NMR investigations have historically been largely relegated to synthetic, Fe-free materials due to complications arising from the introduction of paramagnetic interactions between the NMR nuclei and the unpaired electron(s) on the Fe ions. However, it is becoming increasingly recognized that high-resolution MAS-NMR spectra can be collected from such materials and valuable structural information may be obtained. We present here ^{27}Al and ^{29}Si MAS-NMR spectra of several natural, nearly end-member grossular and pyrope garnets. So-called contact-shifted NMR peaks are observed in most spectra outside the range of expected chemical shifts due to local association of ^{27}Al or ^{29}Si nuclei with paramagnetic $\text{Fe}^{2+,3+}$. A consideration of the possible contact shift mechanisms, the through-space pseudocontact shift and the through-bond Fermi contact shift, has allowed for peak assignments to specific ^{27}Al - or ^{29}Si - $\text{Fe}^{2+,3+}$ coordination environments (i.e. ^{27}Al or ^{29}Si with $\text{Fe}^{2+,3+}$ in the first or second cation coordination sphere). We present here also the results of a ^{27}Al and ^{29}Si MAS-NMR study of a suite of Fe- and Al-bearing MgSiO_3 perovskite samples recovered from high-pressure multi-anvil experiments. MAS-NMR is a useful tool, in this case, to characterize the substitution of Fe^{3+} and Al^{3+} and to address questions of short-range ordering in this important lower mantle phase. It is widely hypothesized that, in many cases, NMR signal loss due to paramagnetic interactions is caused by NMR-active nuclides having paramagnetic ions as nearest or next-nearest neighbors. ^{27}Al NMR signal loss in these MgSiO_3 perovskite samples does not increase linearly with increasing Fe-content suggesting strong local ordering of Fe^{3+} and Al^{3+} into adjacent crystallographic sites. Thus, while the presence of paramagnetic species may introduce complications for MAS-NMR spectroscopy, high-resolution spectra can be collected and a careful analysis of signal loss and the possible presence of contact shifted NMR peaks can potentially provide new structural information for a wide range of synthetic or natural, Fe-bearing geological materials.