



Anomalous peaks in NMR spectra of iron-containing silicate minerals: pseudo-contact shifts and the potential for mapping the distributions of transition metal ions

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High-resolution nuclear magnetic resonance (NMR) spectroscopy has now been applied to problems of mineral structure for more than 25 years. Early attempts to collect MAS spectra on natural minerals rich in iron (or other cations with unpaired electron spins, e.g. more than a few % FeO) showed serious peak broadening, loss of signal, and thus loss of structural information. Spectroscopists have thus largely avoided such materials and have worked either with low-Fe natural minerals (e.g. zeolites) or with Fe-free synthetic compositions. While this problem remains, it has recently become apparent that in silicates with minor contents of such elements (100's to 1000's of ppm), or, in special cases, with much higher contents (at least 4% FeO), NMR spectra of nuclides such as Si-29 and Al-27 may indeed provide interesting and useful structural information that may eventually reveal new details of cation distribution, ordering, clustering, etc. Here we report on the early stages of this new application.

In a recent report (Stebbins, Panero, Smyth and Frost, *Am. Min.* in press) we noted the presence of a variety of tiny "extra" peaks in Si-29 spectra of forsterite and wadsleyite, both containing 10's to 1000's of ppm of transition metal impurities. Some of these have chemical shifts well outside the known range for diamagnetic silicates, and were hypothesized to result from "pseudo-contact" interactions with unpaired electrons, which depend strongly on local structure. Peak shifts of this type have long been known in Sn-119 and Y-89 spectra for oxides such as rare-earth stannates (Grey et al.), but have apparently not been previously reported for silicates.

New data on Si-29 and Al-27 NMR of synthetic pyrope (0.6 % CoO) and natural pyropes from the Dora Maira massif (1.5 to 3.5 wt % FeO) also show "anomalous" resonances, some of which again fall well outside the range of normal chemical shifts (e.g. +140 ppm in a Si-29 spectrum, 70 and 35 ppm in the Al-27 spectrum of a pyrope containing only octahedral Al). The intensities of these peaks correlate well with transition metal contents. Quantitation of spectra suggests that a Si or Al with a paramagnetic cation in the first neighbor cation shell does indeed have its contribution to the total signal "wiped out", but that a second-shell paramagnetic ion can cause a "pseudo-contact" shift of some 10's of ppm that can readily be measured. These effects are strongly dependent on cation-cation distance and on the symmetry of both the NMR-observed nuclide site and that of the transition metal ion. Thus, in a relatively low-symmetry structure such as olivine, multiple "anomalous" peaks are observed because of multiple second cation distances. These rapidly merge into an overall peak broadening as paramagnetic ion content increases above trace element levels. In a higher-symmetry structure such as garnet, the effects are simpler, but if point symmetry is too high (spinel, e.g. ringwoodite), the lack of asymmetry at the transition metal may result in elimination of the contact shift.

As these novel spectroscopic features are explored in other silicate and oxide minerals, it is likely that they will shed new light on cation distributions and structural ordering in systems previously considered to be inaccessible to high resolution NMR methods.