

Toward the wider application of ^{29}Si NMR spectroscopy to paramagnetic transition metal silicate minerals and glasses: Fe(II), Co(II), and Ni(II) silicates

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ABSTRACT

In studies of the structures of silicate minerals and glasses, ^{29}Si NMR spectroscopy has been applied almost exclusively to materials containing relatively low concentrations of ions with unpaired electrons spins, such as most transition metals and rare earths, because of sometimes severe broadening and shifting of resonances in such strongly paramagnetic systems. However, by adapting experimental methods to allow detection of very broad signals, and by examining a much expanded range of frequencies, we show here that accurate spectra can indeed be measured for a series of pure-phase transition metal silicates, including olivines (Fe_2SiO_4 , Co_2SiO_4 , Ni_2SiO_4), Co-akermanite ($\text{CoCa}_2\text{Si}_2\text{O}_7$), and clinopyroxenes ($\text{CoCaSi}_2\text{O}_6$, $\text{NiCaSi}_2\text{O}_6$). For the latter two, we also present data for glasses of the same nominal compositions. For all of these phases, NMR peak broadening is large, in many cases to the point where magic angle spinning (MAS) does not enhance resolution; in all cases the observed paramagnetic shifts fall far outside the known range for diamagnetic silicates. There are clearly large effects of local structure on shift, suggesting great potential sensitivity to variations in chemical, electronic, and magnetic structure in both crystalline and amorphous phases. In particular, the spectra for the glasses are very different from those of crystals in both width and position. In most cases, measured spin-spin relaxation times are long enough to avoid major loss of signal during the NMR acquisition, but this may not always be the case in more magnetically dilute solid solutions, where small, broad paramagnetic resonances due to first cation neighbor interactions may in some systems be difficult to detect. To explore this issue, we present new data on a Ni-doped forsterite ($\text{Mg}_{1.9}\text{Ni}_{0.1}\text{SiO}_4$) and on natural San Carlos olivine ($\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$), which improve upon the accuracy of our previous studies of these materials. It is clear that applications of NMR to paramagnetic silicates holds great promise not only for empirical studies of structure of a much wider range of compositions of minerals and glasses, but for future testing and application of advanced theoretical methods to more completely interpret such results.

Keywords: Nuclear magnetic resonance, contact shift, fayalite, olivine, clinopyroxene, akermanite, transition metal, glass