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 electron 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$_2$SiO$_4$, Co$_2$SiO$_4$, Ni$_2$SiO$_4$), Co-akermanite (CoCa$_2$Si$_2$O$_7$), and clinopyroxenes (CoCaSi$_2$O$_6$, NiCaSi$_2$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 magneto-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 (Mg$_{1.9}$Ni$_{0.1}$SiO$_4$) and on natural San Carlos olivine (Mg$_{1.8}$Fe$_{0.2}$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

**INTRODUCTION**

$^{29}$Si NMR spectroscopy has been widely applied to crystalline and glassy silicates for decades, most commonly with resolution greatly enhanced by magic angle sample spinning (MAS) methods (Engelhardt and Michel 1987; Kirkpatrick 1988; MacKenzie and Smith 2002; Stebbins and Xue 2014). However, nearly all such studies have been of materials with low (less than a few percent) contents of cations with unpaired electron spins, such as most transition metal and rare earth ions, because these can interact strongly with the observed nuclear spins, often leading to severe broadening of spectra even to the point of apparent loss of signal (Grimmer et al. 1983; Hartman et al. 2007; Sherriff and Hartman 1985). This poses an unfortunate gap in our tools to investigate questions of short-range structure and order/disorder, given the wide importance of transition metal, rare earth, and actinide-rich silicates in the Earth sciences and for technology.

Some initial steps have been made in closing this gap by the discovery and quantitation of well-resolved, usually small, $^{29}$Si (and $^{27}$Al) NMR resonances that are displaced well away from typical chemical shifts by relatively low concentrations (ca. 0.1 to 20%) of cations such as Fe$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ in garnets, olivines, zircons, and other minerals (Begaudeau et al. 2012; Dajda et al. 2003; McCarty et al. 2015; Palke and Stebbins 2011b; Palke et al. 2015; Stebbins and Kelsey 2009; Stebbins et al. 2017); analogous observations have been long been known for $^{89}$Y and $^{119}$Sn NMR spectra of rare-earth stannate pyrochlores (Grey et al. 1989, 1990) and have been reported recently for $^{17}$O in MgO and CaO (McCarty and Stebbins 2016b), $^{27}$Al in aluminate garnets (YAG) (George et al. 2013; McCarty and Stebbins 2016a) and $^{31}$P in REE-doped monazites (LaPO$_4$) and xenotimes (YPO$_4$) (Palke and Stebbins 2011a; Palke and Stebbins 2011a; Palke et al. 2013). However, a key part of understanding the complex physics behind such “paramagnetic shifts” must be their measurement in pure-phase end-member compounds (e.g., transition metal silicates), where site occupancies, ordering, and short-range structure are well known, reducing...