Toward the wider application of $^{29}$Si NMR spectroscopy to paramagnetic transition metal silicate minerals: Copper(II) silicates

JONATHAN F. STEBBINS$^{1,*}$

$^{1}$Department of Geological Sciences, Stanford University, Stanford, California 94305, U.S.A.

Abstract

$^{29}$Si NMR has only rarely been applied to silicate minerals in which the predominant cations have unpaired electron spins (e.g., most transition metals and REE), because of the potential for serious line broadening and signal loss. However, as shown here, spectra for a series of natural and synthetic copper(II) silicate minerals can be readily obtained, have paramagnetic shifts far outside known chemical shift ranges, and potentially are very sensitive to structural details involving interactions of paramagnetic cations and Si sites. Signals from different silicon sites in the structures can be distinguished and quantified. Peak broadening due to magnetic couplings and to disorder can be large, but not to the point of "non-observability." NMR signal loss can be related to specific, and in some cases improvable, technical issues such as excitation bandwidth, sample spinning speed, and rapid nuclear spin relaxation. Two samples of the "mineraloid" chrysocolla from different copper ore deposits have very similar spectra with significant paramagnetic shifts, suggesting strong Si-Cu interactions and a common stoichiometry and short-range structure.

Keywords: Nuclear magnetic resonance, unpaired electron spins, diopside, shattuckite, cuprorivaite, planchéite, chrysocolla

Introduction

Since the earliest applications of high-resolution magic angle spinning (MAS) $^{29}$Si NMR to minerals in the late 1970s and early 1980s, nearly all studies have been on materials with low (less than a few percents) contents of paramagnetic cations, whose unpaired electron spins can interact strongly with nuclear spins and can cause severe NMR line broadening, sometimes to the point of making signal difficult or even impossible to observe with conventional methods (Engelhardt and Michel 1987; Grimme et al. 1983; MacKenzie and Smith 2002). This problem (actual or expected) has generally limited application of this powerful experimental technique to groups of minerals with low natural contents of transition metal and rare earth cations (e.g., feldspars, feldspathoids, zeolites, silica polymorphs, clays, white micas, etc.) or to end-members of ferromagnesian solid solutions, often synthetic, with low or no Fe$^{2+}$ or other transition metal cations (e.g., olivines, pyroxenes, amphiboles, high-pressure mantle phases, etc.).

However, paramagnetic interactions can also cause large, but observable, changes in NMR peak positions far outside the ranges for diamagnetic materials, as has been particularly well-studied for $^{6,7}$Li and $^{31}$P NMR in Li-rich transition metal oxides and phosphates of major interest in advanced battery materials (Carlier et al. 2003; Grey and Dupré 2004; Tucker et al. 2002). In such materials, despite paramagnetic shifts of thousands of parts per million and sometimes severe line broadening, both simple MAS NMR and more advanced methods have revealed important new details about ordering of cations, bonding, site symmetries, and other details of short-range structure (Strobridge et al. 2014; Yoon et al. 2004; Zeng et al. 2007). This extended work has led to considerable advances in the theoretical understanding of the complex physics behind such interactions, as well as a rapidly developing ability to calculate paramagnetic shifts from first principles (Clément et al. 2012; Middlemiss et al. 2013).

$^{31}$P MAS NMR for many pure-phase rare earth monazite-type or zircon-type phosphates are also readily observable, again with paramagnetic shifts of up to hundreds of parts per million depending on the number of unpaired spins and details of the electronic structure (Bose et al. 1979; Bregiroux et al. 2007). Pioneering studies of $^{119}$Sn and $^{89}$Y MAS NMR in rare earth stannate pyrochlores introduced this approach to mineralogically interesting oxides (Grey et al. 1989, 1990); very recent studies have reported highly shifted $^{35}$Mg (Lee et al. 2017) and $^{27}$Al (Dogan et al. 2016) resonances in spectra in doped transition metal oxide battery materials and in $^{89}$Y and $^{137}$Ba NMR data for transition metal perovskite phases (Michaelis et al. 2012). Of particular interest in geochemistry are studies of sorbed lithium and phosphate on iron oxyhydroxides, where $^6$Li and $^{31}$P NMR spectra are strongly affected by the host Fe$^{3+}$ cations (Kim et al. 2011, 2008).

In contrast, very few NMR studies of pure-phase paramagnetic transition metal silicates have been reported with a rare exception of early work on Co$_2$SiO$_4$ (Saji et al. 1973). However, recent reports on synthetic olivine and natural garnet solid solutions containing 0.1 to 20% FeO, NiO, or CoO have shown that, at least in such fairly dilute systems, useful resolution can be observed for Si sites with one or two paramagnetic first-neighbor cations, with shifts up to about 400 ppm above the known chemical shift range of –60 to –120 ppm (Begaudeau et