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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, dioptase, shattuckite, cuprorivaite, planchéite, chrysocolla