

Forsterite, hydrous and anhydrous wadsleyite and ringwoodite (Mg₂SiO₄): ²⁹Si NMR results for chemical shift anisotropy, spin-lattice relaxation, and mechanism of hydration

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ABSTRACT

We present a detailed ²⁹Si NMR spectroscopic study of isotopically enriched samples of forsterite and of anhydrous and hydrous wadsleyite and ringwoodite (α , β , and γ phases of Mg₂SiO₄), which complement previous extensive studies of these minerals by XRD and vibrational spectroscopy. ²⁹Si is not detected in any of the phases at levels of about 0.1 to 0.5%. When coupled with recent theoretical calculations on ringwoodite, this suggests the possibility of re-ordering of high-temperature octahedral-tetrahedral disorder during cooling. Cross-polarization (²⁹Si {¹H} CPMAS) NMR supports the protonation of O1 oxygen atoms in hydrous wadsleyite without formation of significant amounts of Si-OH groups. In contrast, new NMR peaks appear in hydrous ringwoodite that cross-polarize very rapidly, indicating very short Si-H distances and the presence of Si-OH, as expected from models in which much of the H⁺ substitutes into Mg²⁺ vacancies. Static NMR spectra provide new constraints on chemical shift anisotropies in wadsleyite and are fully consistent with the cubic structure of ringwoodite. Spin-lattice relaxation in all phases is much better fitted by a stretched exponential function than with a more conventional “T₁” exponential, as expected when relaxation is dominated by paramagnetic impurities. However, the effects of paramagnetic impurity on ion contents on relaxation, and on the formation of newly observed minor peaks that may result from “pseudo-contact shifts,” appear to depend on mineral structure, and will require considerable future study to understand in detail.

Keywords: NMR spectroscopy, forsterite, wadsleyite, ringwoodite, water in mantle