Forsterite, hydrous and anhydrous wadsleyite and ringwoodite (Mg$_2$SiO$_4$): $^{29}$Si NMR results for chemical shift anisotropy, spin-lattice relaxation, and mechanism of hydration

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ABSTRACT

We present a detailed $^{29}$Si NMR spectroscopic study of isotopically enriched samples of forsterite and of anhydrous and hydrous wadsleyite and ringwoodite ($\alpha, \beta$, and $\gamma$ phases of Mg$_2$SiO$_4$), which complement previous extensive studies of these minerals by XRD and vibrational spectroscopy. $^{29}$Si 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 ($^{29}$Si-$^1$H) 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 Mg$^{2+}$ 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 “$T_1$” 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

INTRODUCTION

Forsterite, wadsleyite, and ringwoodite [$\alpha, \beta$, and $\gamma$ phases of (Mg$_{Fe}$)$_2$SiO$_4$] are the most abundant minerals in the Earth’s upper mantle and transition zone (Ita and Stixrude 1992) and thus have been widely studied by many methods to elucidate their structures and geochemical and geophysical properties. The incorporation of H$_2$O into these materials is of particular interest in understanding the water content of the mantle and its ensuing major implications for petrology, global tectonics, and Earth history. The long-range crystal structures of the anhydrous (Fujino et al. 1981; Sasaki et al. 1982) and hydrous (Smyth 1994; Kudoh et al. 1996, 2000; Smyth et al. 1997, 2003) phases are well known from diffraction studies. Infrared and Raman spectroscopy have been especially useful in characterizing O-H vibrations in the hydrous phases, measuring hydroxyl contents and H$_2$O solubilities, evaluating the role of hydrogen bonding, and addressing issues of disorder among proton sites (Kohlstedt et al. 1996; Kudoh et al. 1996, 2000; Kohn et al. 2002; Smyth et al. 2003). However, important details of cation order-disorder, defects, and vacancy structure (all of which may have significant effects on bulk properties including elastic constants) remain uncertain, but are beginning to be addressed by first-principles theoretical calculations (Panero 2008a, 2008b).

Because nuclear magnetic resonance (NMR) spectra are primarily sensitive to short- to intermediate-range structure around particular nuclides and, in principle, can be highly quantitative without matrix-dependent intensity corrections, NMR spectroscopy can serve as an important complement to diffraction methods and other types of spectroscopy. As reviewed recently (Stebbins and Kanzaki 1990; Stebbins 1995; Phillips et al. 1997; Ashbrook et al. 2005; Xue et al. 2008), NMR of the Mg$_2$SiO$_4$ phases, as well of other high-pressure Mg silicates, has been investigated in considerable detail. These have included magic angle spinning (MAS), static, and even single-crystal $^{29}$Si and $^{25}$Mg NMR on forsterite (Derighetti et al. 1978; Weiden and Rager 1985; Stebbins 1997; Ashbrook et al. 2005), $^{29}$Si MAS NMR on wadsleyite and ringwoodite (Stebbins and Kanzaki 1990; Ashbrook et al. 2005), $^{17}$O MAS and multiple-quantum NMR on forsterite, wadsleyite, clinohumite, and chondrodite (Mueller et al. 1990; Ashbrook et al. 2001, 2005) and $^1$H NMR on hydrous wadsleyite (Kohn et al. 2002). NMR studies of related high-pressure Mg silicates have ranged from MgSiO$_3$ perovskite and akimotoite (Stebbins and Kanzaki 1990; Kirkpatrick et al. 1991; Stebbins et al. 2006; Ashbrook et al. 2007a), to majorite garnet and its solid solutions (McMillan et al. 1989; Phillips et al. 1992), as well as the hydrous 10 Å phase (Welch et al. 2006) and phases A, B, D, E, and superhydrous B (Kanzaki et al. 1992; Xue et al. 2008). Forsterite, doped with varying concentrations of paramagnetic transition metal cations (either naturally or experimentally), has also served as a convenient test system...
for evaluating the effects of such impurities on linewidths and in constraining models of spin lattice relaxation (Grimmer et al. 1983; Hartman et al. 2007), both of which can be of critical importance in quantifying NMR results.

Relatively recent developments in NMR technology, including fast-spinning MAS probes with small sample volumes, and progressively higher-field NMR magnets, have facilitated data collection for the small (2–20 mg), high-pressure samples typically produced in multi-anvil apparatus. For $^{29}$Si spectra, enrichment from natural abundances of 4.7% to as high as 95 or 99% can greatly improve spectra. Very recently, we presented such data on several samples of anhydrous forsterite, wadsleyite, and ringwoodite (Stebbins et al. 2009). There, we concluded that $^{29}$Si, anticipated to be present due to Mg-Si disorder in the spinel-structured ringwoodite at high temperature, could not be detected at the 0.1 to 0.5% level, suggesting the possibility of re-ordering during quench. We also showed the presence of several small NMR peaks in forsterite and wadsleyite whose chemical shifts are far outside the known range for Si in silicates, and hypothesized that these were the consequence of "pseudo-contact shifts" resulting from trace paramagnetic impurities. In this paper, we extend the study to hydrous wadsleyite and ringwoodite, and present detailed results on static (non-spinning) spectra, the effects of paramagnetic ions on spin-lattice relaxation, and results from Si{$[^1]$H} cross-polarization (CPMAS) NMR that help to constrain the substitution mechanisms for H$_2$O.

**EXPERIMENTAL METHODS**

**Sample synthesis and characterization**

Synthesis and characterization of the anhydrous materials was described previously (Stebbins et al. 2009). To summarize here, >99% $^{29}$Si-enriched forsterite (Mg$_3$SiO$_4$) starting material was made by grinding together MgO and $^{29}$SiO$_2$ reagents, then heating for 7–12 days at 1500 °C, with several intermediate grinding steps. One batch was made with 0.2 wt% CoO$_2$ (which decomposes to CoO at high temperature) added to speed spin-lattice relaxation ("Fo-1"); this was ground even more thoroughly and re-annealed ("Fo-2") to evaluate the effects of further dispersion of the paramagnetic impurities. A second undoped batch ("Fo-noCo"), as well as a sample with natural isotopic abundance ("Fo-unen," 4.7% $^{29}$Si) were made by similar methods. $^{29}$Si-enriched samples were prepared with a small excess of MgO.

High-pressure syntheses were done at the Bayerisches Geoinstitut, using the 5000 ton multi-anvil apparatus (Frost et al. 2004). For the anhydrous samples, two runs were made with Fo-1 in unequal 2 mm diameter Re foil capsules, at nominal pressure and temperature of 21 GPa and 1500 °C. The first yielded a sample that was mostly ringwoodite ("RWD"); an apparent temperature over-run in the second produced a sample that was mostly wadsleyite ("WDS"). A third experiment at 21 GPa and 1300 °C, on Fo-noCo produced a sample that was mostly ringwoodite ("RWD-noCo"). Hydrous wadsleyite ("WDS + H$_2$O") and hydrous ringwoodite ("RWD + H$_2$O") were prepared from the Fo-1 starting material mixed with Mg(OH)$_2$, to give nominal total water contents of about 1.25 wt%, then welded into Pt capsules.

The wadsleyite was heated for 3 h at 16 GPa, 1200 °C, the ringwoodite for 3 h at 20 GPa, 1300 °C. The hydrous wadsleyite sample contained a small amount of phase B, as detected by NMR (see below) and EPMA; in the hydrous ringwoodite sample the only obvious other phase detected by NMR was a trace of phase B.

Most samples were analyzed for major and several key minor elements by electron microprobe. As summarized in Table 1, all of the average overall compositions were close to the nominal stoichiometry of Mg$_3$SiO$_4$ with a small excess of MgO as planned for the $^{29}$Si-enriched materials. Relatively large standard deviations may reflect the fine particle size of several of the samples and resulting imperfect polish, and/or the presence of small inclusions of MgO. In the hydrous samples, slightly more excess MgO was expected because of the added Mg(OH)$_2$. We did not obtain EPMA data on the hydrous ringwoodite sample because of its small size. Several inclusions with the composition of phase B [Mg$_3$Si$_2$O$_5$(OH)$_2$, 65 wt% MgO, 32 wt% SiO$_2$] were detected by EPMA in the hydrous wadsleyite, as well as in the NMR spectra. These were excluded from the average composition given in Table 1. Any variations in Mg/Si, caused by incorporation of H$_2$O, were not obvious given the uncertainties of the analyses. Traces of CaO, a common impurity in MgO reagents, may be present just above the detection limit of about 0.02 ± 0.02 wt%; FeO, another common impurity of special interest in some aspects of the NMR spectra, was not significantly detected at a similar limit. CoO was detected, and was significantly higher in the doped than in the undoped samples, at roughly 0.06 ± 0.02 wt%. These values were considerably less than the added dopant level of about 0.2 wt%, indicating some loss during synthesis. Estimated contents of other paramagnetic trace element cations, summing contributions from analyzed starting materials, include about 20 ppm Fe (by weight), 10 ppm each of Ni and Cr, and 60 ppm Cu.

Powder XRD on the Co-doped ringwoodite detected only this phase plus 5% wadsleyite. Unit-cell parameters of the hydrous ringwoodite and hydrous wadsleyite were determined by single-crystal X-ray diffraction. A single crystal of the hydrous ringwoodite was oriented using a Bruker APEX II CCD diffractometer and the unit-cell parameter refined from the centering parameters of 48 X-ray reflections using a point detector on a Bruker P4 diffractometer. The refined cell parameter was $a = 8.0702(5)$ Å, giving a unit-cell volume of 525.59(11) Å$^3$, indicating an H$_2$O content of 1.0 ± 0.08 wt% (Smith et al. 2007). Similarly, the cell parameters of the hydrous wadsleyite were refined from the centering of 58 X-ray reflections as $a = 5.6599(10)$ Å, $b = 11.4572(7)$ Å, $c = 8.2540(14)$ Å, $V = 538.6(2)$ Å$^3$. This gave a $b/a$ ratio of 2.0114 indicating an H$_2$O content of 0.27 ± 0.03 wt%

| TABLE 1. | Electron microprobe data summary |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Fo-unen | Fo-1   | Fo-noCo | RWD   | RWD-noCo | WDS   | WDS + H$_2$O |
| SiO$_2$        | 43.3(1.1) | 43.3(0.4) | 42.5(1.4) | 42.9(0.4) | 42.4(0.6) | 42.8(0.7) | 43.3(0.9) |
| MgO            | 57.9(0.8) | 58.5(0.6) | 59.0(1.7) | 57.4(0.9) | 58.2(0.8) | 58.3(1.1) | 58.4(0.7) |
| FeO            | 0.03(0.02) | 0.02(0.02) | 0.01(0.01) | 0.02(0.02) | 0.02(0.02) | 0.01(0.02) | 0.02(0.01) |
| CaO            | 0.08(0.02) | 0.03(0.01) | 0.04(0.01) | 0.02(0.01) | 0.02(0.01) | 0.01(0.01) | 0.02(0.01) |
| CoO            | 0.00(0.01) | 0.10(0.02) | 0.01(0.02) | 0.05(0.02) | 0.02(0.02) | 0.06(0.03) | 0.04(0.02) |
| Totals         | 101.3(1.6) | 101.9(0.9) | 101.7(1.7) | 100.5(1.2) | 100.1(1.3) | 101.2(1.4) | 101.8(0.4) |
| SiO$_2$        | 33.4      | 32.8    | 32.3    | 33.1    | 32.5    | 32.7    | 32.8    |
| MgO            | 66.6      | 67.2    | 67.7    | 66.9    | 67.5    | 67.3    | 67.2    |

Notes: Standard deviations shown in parentheses; each analysis is the average of 8–12 data points. All samples except "Fo-unen" are $^{29}$Si enriched; all enriched samples are Co-doped unless labeled "noCo." Fo = forsterite, RWD = ringwoodite, WDS = wadsleyite.
saturate the magnetization, which was then allowed to recover for a time period \(\tau\) and measured with a 90° observe pulse. \(^{29}\text{Si}(1\text{H})\) cross-polarization magic-angle spinning spectra (CPMAS) were collected with constant-amplitude 1H CP pulses (75 kHz) and 1H decoupling (50 kHz) during observation, with acquisition times of 41 ms, contact times from 0.2 to 20 ms, and spinning rates of 3.5 kHz. Pulse delays of 2 to 8 s were used, and generally 8000 transients were collected for each spectrum. Cross-polarization data were also collected on a sample of high-purity natural talc, which was also useful for optimizing experimental conditions.

**RESULTS AND DISCUSSION**

**MAS NMR spectra**

Peak positions, widths, and relative areas for \(^{29}\text{Si}\) spectra are listed in Table 2, and selected spectra are shown in Figures 1 and 2. The \(^{29}\text{Si}\) MAS spectra for the forsterite samples, and for the anhydrous wadsleyite and ringwoodite samples, are described in our initial report (Stebbins et al. 2009). To briefly summarize, the very high signal-to-noise ratio obtained from the isotopic enrichment resulted in a detection limit of \(^{1}\text{Si}\) in the ringwoodite of about 0.1 to 0.5%. However, this species was not detected. Given recent theoretical predictions of 2 to 4% \(^{1}\text{Si}\) at the temperatures of synthesis (Panero 2008a), this suggested that re-ordering may occur during cooling, as has been observed at high temperatures for MgAl\(_2\)O\(_4\) spinel (Wood et al. 1986; Redfern et al. 1999). The contents of \(^{1}\text{Si}\) (up to 5% of the total Si) suggested by earlier single-crystal XRD studies of anhydrous and hydrous ringwoodite (Hazzen et al. 1993; Kudoh et al. 2000) are much higher than this detection limit, and those results thus seem inconsistent with the NMR data. This may reflect the close similarity in X-ray scattering of Si and Mg. It is also possible that if re-ordering does occur during quench, defects or vacancies may remain that could affect long-range average polyhedral volumes and thus the interpretation of the X-ray structure. And, of course, there remains the possibility that ringwoodite samples synthesized at different temperatures and with different cooling rates from those studied here might contain greater amounts of quenched-in Si-Mg disorder.

Also in ringwoodite, several small peaks, which relax at a rate similar to the main peak and correspond to no known phases (labeled \(X_1\), \(X_2\), and \(X_3\) in Figs. 1 and 2) were observed, which we speculated could be related to defects generated during this re-ordering process or residual from high-temperature disorder. \(X_3\) is present for the Co-doped anhydrous and hydrous ringwoodite, but not in the Co-free sample, for unknown reasons. In addition, in the forsterite and wadsleyite samples, but not in ringwoodite, several very small, fast-relaxing “extra” peaks were detected (arrows in Fig. 2), many of which have chemical shifts well outside the known ranges of \(^{29}\text{Si}\) chemical shifts in silicates. We suggested that these are likely to be caused by “pseudocontact shifts,” resulting from through-space dipolar interactions with trace impurities of paramagnetic ions (Grey et al. 1989, 1990). The added Co\(^{2+}\); however, was apparently not the cause of these unusual features, but did increase peak widths significantly and speed relaxation rates as planned in the experimental design (see below). Other paramagnetic trace element cations could be the source of these features [e.g., Fe, Ni, Cr, and Cu known to be present in the starting materials at the level of 10 to 60 ppm (Stebbins et al. 2009)], but only systematic studies of effects of trace element doping on spectra will be able to confirm this hypothesis. Future studies of the temperature dependence of such shifted frequencies may also be useful for distinguishing pseudocontact effects from through-bond Fermi contact shifts (Grey et al. 1990).

As in our previous report, spectra were collected over wide ranges of pulse delays, from 0.2 to 1800 or even 3600 s. With one minor exception noted below for the RWD + H\(_2\)O, no additional features were seen in the longer-delay, more fully relaxed, spectra. In most cases we thus present partially saturated spectra.
collected at delay times of 1 to 10 s, to accentuate signal-to-noise and also to highlight minor, fast-relaxing features. Figure 1 shows the $^{29}$Si regions of the spectra for the three ringwoodite samples. As noted previously, the anhydrous samples contain minor amounts of wadsleyite, as well as the possible “defect” peaks $X_1$ and $X_2$. The hydrous sample contains neither of these minor features, but has instead two other small peaks at −77.5 and −79.7 ppm, which we denote $R_{H1}$ and $R_{H2}$. By subtracting a fit of the main peak from the experimental spectrum, we estimate the sum of the areas of these components is roughly 4 ± 2% of the total Si, in spectra with both short (1 s) and long (300 s) pulse delays. As discussed below, these are greatly enhanced in the cross-polarization (CPMAS) spectra, and thus must represent Si sites that are especially close to the protons in the hydrous material. The $^{29}$Si regions for the one-pulse spectra of the wadsleyite samples are shown with the CPMAS data below.

In Figure 2, a wider frequency range is shown, with vertical scales enlarged about 20 to 40× those shown in Figure 1. Here, the “extra” peaks, apparently related to paramagnetic impurities, are clearly seen for the Fo-noCo sample, for both the anhydrous and hydrous wadsleyite, but not for the ringwoodite samples. We suggested previously (Stebbins et al. 2009) that this difference could be the consequence of the much higher symmetry of the latter. In the hydrous wadsleyite, four small peaks are seen at −64.1, −75.1, −75.8, and −170.4 ppm, which correspond well to those previously reported for phase B [$\text{Mg}_{12}\text{Si}_4\text{O}_{19}(\text{OH})_2$] (Phillips et al. 1997). From the fully relaxed spectrum, we estimate that about 6% of the Si in this sample is in phase B, and that the $^{29}$Si peak abundance of phase B in the latter is much smaller, totaling about 0.2 to 0.6% of the Si in relaxed, long-delay spectra. In both hydrous ringwoodite and hydrous wadsleyite samples, the phase B peaks are greatly enhanced in the CPMAS spectra as expected from its high H content (see figures later in paper).

Figure 2a also shows the spectrum collected with a 300 s delay for RWD + H$_2$O. Here, a tiny, sharp peak at −180.7 ppm is probably within uncertainties of that reported for akimotoite (−181.0 ppm (MgSiO$_3$) (Stebbins and Kanzaki 1990). The peak area leads to an estimate of about 0.5 ± 0.2% of total Si in this phase. This peak is not visible in the shorter delay spectra with much higher signal-to-noise ratios and thus much lower detection limits, which implies that it is present in a separate phase with a slower spin-lattice relaxation rate than that of the ringwoodite. If the peak is due to akimotoite, it may be related to the formation of the minor amount of phase B, or may suggest some minor compositional heterogeneity in this sample. The $^{29}$Si peak could, of course, result instead from a small amount of residual site disorder in the ringwoodite and only coincidentally resemble the spectrum of akimotoite, but the apparent difference in relaxation rate could be difficult to explain.
Static spectra

Non-spinning (static) spectra are a straightforward way to constrain the magnitude and symmetry of the chemical shift anisotropy (CSA), although analyses of spinning sideband patterns for slow MAS experiments often give good results as well (Smith et al. 1983). Representative static spectra for forsterite, wadsleyite, and ringwoodite are shown in Figures 3 and 4. Forsterite is an interesting test case, as it has been unusually well studied by NMR, including rare single-crystal measurements and detailed theoretical calculations, as reviewed recently (Ashbrook et al. 2007b, 2007c). Our results agree well with a previous static spectrum for a sample with natural isotopic abundance, which in turn was accurately predicted by density functional theory (CASTEP) calculation, yielding best estimates of the anisotropy $\Delta_{\text{cs}}$ of 29.3 ppm and asymmetry parameter $\eta$ of 0.61 as defined previously; fits to the experimental spectrum yielded 32.3 ppm and 0.57 (Ashbrook et al. 2007b, 2007c). The calculation was based on the optimization of the X-ray structure of an olivine near to Fo90 in composition (Brown 1970). Our spectrum for isotopically enriched forsterite may be slightly broadened by Si-Si dipole-dipole couplings (expected to be a few hundred Hertz), and is best fitted with slightly different parameters, with $\delta_{\text{iso}}$ from the MAS data at $-61.8$ ppm, $\Delta_{\text{cs}} = 32.3 \pm 0.5$ ppm, and $\eta = 0.70 \pm 0.05$, convolved with a Gaussian broadening function of about 500 ± 200 Hz FWHM. For wadsleyite, this same theoretical approach (Ashbrook et al. 2007b) yielded $\delta_{\text{iso}} = -80.0$ ppm, $\Delta_{\text{cs}} = -40.5$ ppm, and $\eta = 0.11$. These give a reasonably good prediction of the experimental peak shape (Fig. 4), which is, however, better fitted by a somewhat narrower CSA, with $\delta_{\text{iso}}$ from the MAS data at $-78.7$ ppm, $\Delta_{\text{cs}} = -37.0$ ppm, and $\eta = 0$ to 0.1, with a Gaussian broadening of about 1000 Hz. The sign of $\Delta_{\text{cs}}$ and the near-axial symmetry ($\eta \approx 0$) are sensible for a Q1 silicate where the longest Si-O bond is generally to the bridging oxygen (Grimmer et al. 1981).

In the spectrum for anhydrous wadsleyite, the narrow additional peak in the center is due to the minor ringwoodite component, as confirmed by static spectra of the three samples of this phase. For all of the latter, peaks are symmetrical, roughly Gaussian in shape (although having minor Lorentzian “tails”), with FWHM of 760 Hz (9.5 ppm). The Co doping caused little or no broadening of the static line shape. The cubic symmetry of this mineral indicates that the CSA should be 0, consistent with observation. Some of the residual peak width can be attributed to Si-Si dipolar coupling. From the structure (Sasaki et al. 1982) and a simple “Van Vleck” summation of $1/r^4$ for the second moment (Abragam 1961; MacKenzie and Smith 2002), the dipolar linewidth can be calculated as about 400 Hz, leaving the remaining width for minor contributions from other factors such as paramagnetic impurities and/or slight disorder. A similar conclusion was reached for $^{29}$Si-enriched MgSiO$_3$ perovskite (Kirkpatrick et al. 1991).

CPMAS data and H site characterization

In the cross-polarization NMR experiment, nuclear spin energy is transferred from $^1$H to $^{29}$Si nuclei. As discussed in detail in several recent CPMAS studies of hydrous silicates (Phillips et al. 1997; Oglesby and Stebbins 2000; Xue et al. 2008), the efficiency of this process is enhanced by the number of close $^1$H neighbors to a given Si site, depends strongly on their distance ($1/r^2$), and is affected in complex ways by dynamics and by relaxation of the $^1$H spin system. Although extraction of structural information from CPMAS spectra can be difficult and generally non-quantitative, such data can provide useful constraints on relative Si-H distances when comparing sites in similar materials. Because of the strong enhancement of signals from Si in stoichiometrically hydrous phases or from Si relatively close
M(CP) = M0[(1 - TsiH/T1H)] [exp(-t/TSiH) - exp(-t/T1H)]

Here, the derived parameters are M0, which is the limiting, infinite time value for the CP magnetization, TsiH, the exponential time constant for the growth of the observed 29Si signal, and T1H, that for the decay of the 1H magnetization during the pulse sequence, which in turn may eventually begin to reduce the observed signal. For most of the sites for most of the samples observed here, the latter was long enough to be only roughly estimated, not directly derived from regression of the data. However, this does not greatly affect estimates of the more structurally interesting TsiH. Fitted curves for the phase B peaks in the hydrous wadsleyite sample, and the sum of the main wadsleyite peak and the WH1 shoulder, are shown in Figure 6, with derived parameters in Table 3. Separation of the two wadsleyite components by fitting was not very robust because of their strong overlap. However, the two derived TsiH values do at least qualitatively reflect the clearly observed differences in their growth rate with contact time as seem in Figure 5.

As shown in the table, the measured TsiH values for phase B are systematically smaller than those reported previously (Phillips et al. 1997), probably because of differences in sample spinning rate and pulse sequence used. Nonetheless, the relative sizes of TsiH for the four peaks are similar between the two studies, supporting at least a rough correlation with closest Si-H distance in this mineral as previously documented (Phillips et al. 1997). The B1 and B2 peaks have the longest TsiH values in both studies, although in our results these values are the same within error. The corresponding sites have the longest Si-H distances as previously documented (Phillips et al. 1997), probably because of differences in sample preparation and handling.

For example, comparing data for WDS + H2O for t = 1 vs. 6 ms (Fig. 5), it is obvious that the phase B peaks grow in at different rates, as studied in detail previously in a sample composed primarily of this mineral (Phillips et al. 1997). It is also clear that the main wadsleyite peak at ~78.7 ppm (W) grows more slowly than a shoulder at ~78.1 ppm (WH1), suggesting that the latter is a minor component (not obvious in the one pulse spectra because of its low intensity) representing Si that are closer than average to included 1H.

Detailed analysis of results required fitting of spectra to extract the areas of overlapping components. This was done for each of the two hydrous samples by first fitting the spectra at the longest contact times, which generally had the most intense peaks, and then fitting the remainder of the spectra with resulting peak positions, widths, and shapes (Gaussian fractions) as constraints. This provided more robust fits of the noisier data at shorter contact times, although residuals are somewhat greater than less-constrained fits. Plots of magnetization (fitted peak areas, M) vs. contact time can then be analyzed with a well-known equation for the sum of exponential growth and exponential decay, which is often a good approximation in systems of this type (dilute spins, static protons) (Phillips et al. 1997):

\[ M(t) = M_0 (1 - T_{siH}/T_{1H}) \left[ \exp(-t/T_{siH}) - \exp(-t/T_{1H}) \right] \]

Figure 5 illustrates representative CPMAS spectra for the hydrous wadsleyite sample, compared with MAS (non-CP, often denoted as “1 pulse”) spectra for the hydrous and anhydrous samples. As noted above, the latter (only) contains a minor ringwoodite component. Also as noted above, the MAS spectra of the hydrous wadsleyite reveal four extra peaks (B1–4) known to be due to phase B (Phillips et al. 1997), which are greatly enhanced in the CPMAS spectra. Other than the 29Si peak for phase B (B1 in Fig. 2), no signals for octahedral Si were seen in any of the CPMAS spectra, which had typical signal-to-noise ratios of about 180 (WDS + H2O) to 40 (RWD + H2O). In the CP experiment, the energy transfer from 1H to 29Si takes place during a “contact time” (tc), which was adjusted within the range of about 0.2 to 20 ms. As this time is increased, the observed 29Si magnetization gradually builds up, at a rate related most strongly to H in nominally anhydrous phases with minor water contents, CPMAS spectra can often also provide insights into the presence of minor components.

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\[ M(t) = M_0 (1 - T_{siH}/T_{1H}) \left[ \exp(-t/T_{siH}) - \exp(-t/T_{1H}) \right] \]

Here, the derived parameters are M0, which is the limiting, infinite time value for the CP magnetization, TsiH, the exponential time constant for the growth of the observed 29Si signal, and T1H, that for the decay of the 1H magnetization during the pulse sequence, which in turn may eventually begin to reduce the observed signal. For most of the sites for most of the samples observed here, the latter was long enough to be only roughly estimated, not directly derived from regression of the data. However, this does not greatly affect estimates of the more structurally interesting TsiH. Fitted curves for the phase B peaks in the hydrous wadsleyite sample, and the sum of the main wadsleyite peak and the WH1 shoulder, are shown in Figure 6, with derived parameters in Table 3. Separation of the two wadsleyite components by fitting was not very robust because of their strong overlap. However, the two derived TsiH values do at least qualitatively reflect the clearly observed differences in their growth rate with contact time as seem in Figure 5.

As shown in the table, the measured TsiH values for phase B are systematically smaller than those reported previously (Phillips et al. 1997), probably because of differences in sample spinning rate and pulse sequence used. Nonetheless, the relative sizes of TsiH for the four peaks are similar between the two studies, supporting at least a rough correlation with closest Si-H distance in this mineral as previously documented (Phillips et al. 1997). The B1 and B2 peaks have the longest TsiH values in both studies, although in our results these values are the same within error. The corresponding sites have the longest Si-H distances as previously documented (Phillips et al. 1997), probably because of differences in sample preparation and handling.

For example, comparing data for WDS + H2O for t = 1 vs. 6 ms (Fig. 5), it is obvious that the phase B peaks grow in at different rates, as studied in detail previously in a sample composed primarily of this mineral (Phillips et al. 1997). It is also clear that the main wadsleyite peak at ~78.7 ppm (W) grows more slowly than a shoulder at ~78.1 ppm (WH1), suggesting that the latter is a minor component (not obvious in the one pulse spectra because of its low intensity) representing Si that are closer than average to included 1H.

Detailed analysis of results required fitting of spectra to extract the areas of overlapping components. This was done for each of the two hydrous samples by first fitting the spectra at the longest contact times, which generally had the most intense peaks, and then fitting the remainder of the spectra with resulting peak positions, widths, and shapes (Gaussian fractions) as constraints. This provided more robust fits of the noisier data at shorter contact times, although residuals are somewhat greater than less-constrained fits. Plots of magnetization (fitted peak areas, M) vs. contact time can then be analyzed with a well-known equation for the sum of exponential growth and exponential decay, which is often a good approximation in systems of this type (dilute spins, static protons) (Phillips et al. 1997):

\[ M(t) = M_0 (1 - T_{siH}/T_{1H}) \left[ \exp(-t/T_{siH}) - \exp(-t/T_{1H}) \right] \]

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fraction of Si with a somewhat shorter distance, perhaps about 0.28 nm. These distances are thus typical of those seen for Si sites near to Mg-OH groups in hydrous Mg silicates, and are considerably longer than is typical for “Si-OH” groups in silicates (Oglesby and Stebbins 2000). Thus, the NMR results provide general support for the prevalent model of most H in hydrous wadsleyite being bonded to the O1 oxygen, which is otherwise bonded only to Mg (Smyth 1994; Kudoh et al. 1996; Smyth et al. 1997). The $^{29}$Si NMR data do not, however, shed much light on uncertainties in exact proton positions, proton site order/disorder, or extent of H-bonding. Further studies with $^1$H NMR (Phillips et al. 1997; Kohn et al. 2002) and $^{29}$Si-$^1$H double resonance methods (Xue et al. 2008) may help provide such details.

CPMAS results for the hydrous ringwoodite are dramatically different from those for wadsleyite. As shown in Figure 7, some phase B is present, again with peaks accentuated relative to the one-pulse data but considerably smaller than in the hydrous wadsleyite, as expected from their much smaller contribution to the MAS spectra. Again comparing spectra with relatively short (1 ms) vs. relatively long (6 ms) contact times, it can be seen that two new peaks grow in very rapidly. These were seen as small features in the one-pulse spectra, RH1 and RH2. Their positions bracket the W and WH1 peaks in hydrous wadsleyite (also shown in Fig. 6 for comparison), and are thus clearly distinct. Their chemical shifts correlate with no known hydrous magnesium silicates, most of which have been previously studied by NMR (see introduction). Their displacement of several parts per million from the main ringwoodite peak (R) suggests a significant

designation does not imply that the oxygen involved is bonded only to one Si and one H. In fact, in silicates with such groups, there are generally one or more additional mono- or divalent cation neighbors (Oglesby and Stebbins 2000). New CPMAS data were collected on a sample of natural talc [Mg$_3$Si$_4$O$_{10}$(OH)$_2$] using identical methods to those applied to the high-pressure phases. Talc also has Mg-OH groups and an Si-H distance slightly longer than that for Si3 in phase B, and yields a T$_{Si-H}$ value that is slightly longer than that observed for the B1 peak. We conclude that the mean value of T$_{Si-H}$ for the W + WH1 peaks in hydrous wadsleyite (3.3 ms) corresponds to a mean closest Si-H distance of roughly 0.3 nm. The WH1 shoulder may represent a smaller fraction of Si with a somewhat shorter distance, perhaps about 0.28 nm. These distances are thus typical of those seen for Si sites near to Mg-OH groups in hydrous Mg silicates, and are considerably longer than is typical for “Si-OH” groups in silicates (Oglesby and Stebbins 2000). Thus, the NMR results provide general support for the prevalent model of most H in hydrous wadsleyite being bonded to the O1 oxygen, which is otherwise bonded only to Mg (Smyth 1994; Kudoh et al. 1996; Smyth et al. 1997). The $^{29}$Si NMR data do not, however, shed much light on uncertainties in exact proton positions, proton site order/disorder, or extent of H-bonding. Further studies with $^1$H NMR (Phillips et al. 1997; Kohn et al. 2002) and $^{29}$Si-$^1$H double resonance methods (Xue et al. 2008) may help provide such details.

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![Figure 7.](image-url)
difference in their first cation coordination shells, for example the substitution of H$^+$ for Mg$^{2+}$. The appearance of two discrete new peaks also suggests complexities to the substitution mechanism, which may eventually be elucidated by theoretical calculations or further experiments.

In plots of peak area vs. contact time (Fig. 8), the RH$_1$ and RH$_2$ peaks clearly grow in much faster than any of the phase B peaks or those in wadsleyite; they can also be seen to begin to “decay,” due to relatively short T$_{SIH}$ values. There is a strong implication of particularly short nearest Si-H distances, as the T$_{SIH}$ values are extremely short, about 1 ms. These peaks are probably due to Si with direct links to H, i.e., “Si-OH” groups as defined above. If these Si sites are indeed part of the hydrous ringwoodite structure, this is just what would be expected if H incorporation primarily involves the Mg$^{2+}$ = 2H$^+$ mechanism. Unless there are Si vacancies or $^{29}$Mg defects, all O in the structure are bonded to one Si, thus each added H must be part of an “Si-OH” linkage. The predominance of this mechanism is supported by detailed X-ray diffraction studies, which generally show that most or all cation vacancies are at octahedral sites (Kudoh et al. 2000; Smyth et al. 2003).

Quantifying populations of species from CPMAS spectra is problematical because of the complexities of cross-polarization dynamics. However, the RH$_1$ and RH$_2$ peaks from the one-pulse experiments can be analyzed with more confidence. If each of the Si represented by these peaks is assumed to account for one H, then their 4 ± 2% combined area implies 0.04 moles of H per mole of Mg$_2$SiO$_4$ or about 0.25 ± 0.12 wt% H$_2$O. This figure is well below the nominal water content of 1.25 wt% and the uppermost curve.

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Spin-lattice relaxation

The high-signal to noise ratios provided by the $^{29}$Si enrichment, together with narrow NMR peaks, facilitated a relatively detailed study of the spin-lattice relaxation behavior of all of the samples. In the “saturation-recovery” experiment used here, an initial train of pulses saturates the magnetization. After a relaxation delay time $\tau$, the re-growth of the magnetization, caused by spin-lattice relaxation, is measured with an “observe” pulse. $\tau$ from 0.2 to 1800 s were explored. Representative data for the resulting peak areas, normalized to values at the longest delays, are shown with linear scales in Figure 9. Results for all samples are displayed on a log-log plot in Figure 10 to better display the initial relaxation curves. The trends of the data, as well as fitted curves discussed below and comparison of absolute intensities scaled by sample weight, indicate that the magnetization is usually at least 95% recovered after a delay of 1800 s. In the case of the ringwoodite samples containing minor wadsleyite (and vice versa), peaks were fitted to obtain areas for the major phases.

In systems with rapid physical diffusion (e.g., liquids) or rapid spin diffusion, spin-lattice relaxation generally follows a simple exponential behavior, with

$$M(\tau) = M_0 \{1 - \exp\left[-\left(\tau/T_1\right)\right]\}$$

where $M_0$ is the fully recovered observed magnetization (z-component) and $T_1$ is the “relaxation time” for all spins in the sample (Abragam 1961). (Spin diffusion involves the exchange of energy via dipolar coupling between nuclear spins that are abundant, relatively close, and of relatively high gyromagnetic ratios $\gamma$, e.g., $^1$H in organic materials or $^{19}$F in fluorides.) However, in solid materials where both physical and spin diffusion are slow, notably rigid oxide materials without abundant, high-$\gamma$ spins, the relaxation of spin 1/2 nuclei (e.g., $^{29}$Si) is often dominated by direct, through-space dipolar couplings between the observed nuclei and the much stronger magnetic dipoles associated with unpaired electron spins (Hartman et al. 2007), for example on paramagnetic impurity cations such as Fe$^{2+}$ or Co$^{2+}$ in the samples.
It has been shown (Tse and Hartmann 1968; Hayashi 1994; Hartman et al. 2007) that in this common case, relaxation is much better described by a “stretched” exponential, with:

$$M(\tau) = M_\infty \{1 - \exp[-(\tau/T')^n]\}$$ (3)

whereas those very far from any impurity may relax very slowly. Some nuclear spins that happen to be very close to an impurity will relax very rapidly, because the effect of such a dipolar coupling scales as the inverse sixth power of the distance from the nuclide to the electron spin, in the case of dilute impurities there will generally be a wide range of distances and thus a wide range of relaxation rates throughout the sample. That is, some nuclear spins that happen to be very close to an impurity will relax very rapidly, whereas those very far from any impurity may relax very slowly. It has been shown (Tse and Hartmann 1968; Hayashi 1994; Hartman et al. 2007) that in this common case, relaxation is much better described by a “stretched” exponential, with:

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Ideally, n should be 0.5, but a mixture of the behaviors given in Equations 2 and 3 can result in fitted exponents between 0.5 and 1.0 (Hartman et al. 2007; Malfait et al. 2008).

For simplicity and to allow direct comparisons of the two equations with the same number of adjustable parameters, we fixed n = 1 or 0.5 and fitted each data set with only two parameters, either $$M_\infty$$ and $$T_1$$ (Eq. 2) or $$M_\infty$$ and $$T'$$ (Eq. 3). Peaks areas (normalized to data at the longest observed $$\tau$$) vs. relaxation delays (not logs) were fitted by non-linear least-squares regression; typical fits are shown for two of the samples with both the linear (Fig. 9) and log-log scales (Fig. 10). As expected from several relaxation time studies, including detailed work on transition-metal doped forsterite (Hartman et al. 2007), Equation 3 gives much better fits; derived parameters are listed in Table 4. For most samples, fitted $$M_\infty$$ values are only 1 to 4% higher than the data at the longest observed $$\tau$$, suggesting nearly complete relaxation by 1800 s. However $$M_\infty$$ reaches about 9% above $$M_{1800}$$ for the most slowly relaxing sample (Fo-noCo), and is actually slightly below $$M_{1800}$$ for the Co-doped ringwoodite, presumably simply because of fitting uncertainties. The $$T_1$$ fits (Eq. 2 or 3 with n = 1) were poor for all samples ($$\chi^2$$ typically at least 10× worse), especially at short delays: the shapes of the fitted curves are clearly inaccurate, as can be seen in both linear and log-log plots. In Table 4, we include the resulting $$T_1$$ values to facilitate comparisons with other studies, but we re-emphasize that these are poor approximations. Furthermore, fitted $$T_1$$‘s decrease greatly and systematically as the longest $$\tau$$ data are excluded from the fits. This may be one reason why successively more extended studies of relaxation in, for example, SiO2 glass, typically produce longer and longer estimates of $$T_1$$ (Gladden et al. 1986; Malfait et al. 2008). We also note that better stretched exponential fits could be obtained by allowing n to be adjustable and introducing as well another multiplier term (Hartman et al. 2007), but the physical meaning of the extra parameters may not always be obvious.

For the 28Si-enriched forsterite, the Co doping has a large effect on the relaxation, reducing the stretched exponential time constant $$T'$$ by almost an order of magnitude. The curve for the natural abundance forsterite falls in between. It is likely that in the two undoped samples, relaxation is controlled by unknown trace amounts of paramagnetic impurities in the reagents, most likely Fe2+. In contrast, data for all three of the ringwoodite samples, whether Co-doped or not, are close to each other and to the curve for the Co-doped forsterite. Although EPMA data indicate that the Co content of the ringwoodite is somewhat lower than that of its forsterite precursor (possibly through diffusion into the Re high-pressure capsule?), there is clearly a significant effect of

<table>
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<th>Table 4. Fitted parameters for spin-lattice relaxation curves</th>
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<td>Sample</td>
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<tr>
<td>--------</td>
</tr>
<tr>
<td>Fo-noCo</td>
</tr>
<tr>
<td>Fo-2</td>
</tr>
<tr>
<td>Fo-unen</td>
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<tr>
<td>RWD-noCo</td>
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<tr>
<td>RWD</td>
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<td>RWD + H2O</td>
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Notes: Standard errors from fit are shown in parentheses. Magnetization or “M” values fitted by either Equation 1 or 2 (see text) are the integrated or fitted peak areas for the major phase in each sample.
the dopant on the linewidth (Fig. 1). The apparent lack of effect on the relaxation is thus surprising and suggests that Co cannot be dominating the relaxation, perhaps because of structural differences between the phases, e.g., the much higher symmetry of the ringwoodite (spinel) structure than that of the forsterite. It is possible as well that spin diffusion might begin to be important in some of these phases, given the high level of isotopic enrichment, although the spinning rate of 20 kHz is likely to mostly quench this process. Spin diffusion was supported by slow MAS NMR experiments on $^{29}$Si-enriched MgSiO$_3$ perovskite, resulting in rapid, simple exponential relaxation (T$_1$ of only 8 s) (Kirkpatrick et al. 1991). This phase has corner-shared SiO$_4$ octahedra and thus a continuous network for Si-Si spin diffusion with Si-Si distances of 0.343 to 0.345 nm (Horiiuchi et al. 1987). Although Si-Si distances are somewhat longer in both ringwoodite and forsterite because the SiO$_4$ tetrahedra are not directly connected, the closest such distance is somewhat shorter in ringwoodite [3-D network of 0.349 nm Si-Si distances (Sasaki et al. 1982)] than in forsterite (2-D chains of 0.362 nm distances) (Fujino et al. 1981). Both samples of wadsleyite were made from the Co-doped forsterite, and gave almost indistinguishable relaxation curves (Fig. 10). In this phase, pairs of SiO$_4$ tetrahedra are corner-shared (Si-Si distance of 0.298 nm), but there is not a continuous network of close Si neighbors (typical next Si-Si distance of 0.360 nm) (Smalley et al. 1997). Added H$_2$O had little or no effect on the relaxation of either ringwoodite or wadsleyte (Fig. 10), indicating that the $^1$H was too dilute to significantly enhance spin diffusion from $^{29}$Si to paramagnetic centers. Finally, we note that at $<$$< 10^3$ Hz the limiting slope in a log-log plot of Equation 3 becomes 0.5. This is the expected initial slope for relaxation by through-space coupling to paramagnetic impurities, when the spatial distribution is three-dimensional. In materials such as silica gel and nano-scale phase separated Li$_2$SiO$_3$ glasses, this initial slope has been observed to be reduced, indicating a reduced dimensionality (Devreux et al. 1990; Sen and Stebbins 1994).

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