LETTER

Forsterite, wadsleyite, and ringwoodite (Mg$_2$SiO$_4$): $^{29}$Si NMR constraints on structural disorder and effects of paramagnetic impurity ions

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ABSTRACT

We present here high-resolution $^{29}$Si MAS NMR data for synthetic samples of forsterite (α-Mg$_2$SiO$_4$), wadsleyite (β), and ringwoodite (γ). Enrichment to >99% $^{29}$Si provides greatly enhanced signal-to-noise ratios and thus great sensitivity to small features in the spectra. At a detection limit of 0.1 to 0.5%, no six-coordinated Si (VISi) is observed in any of the polymorphs, although these results could be consistent with theoretical predications of 1 to 2% Mg-Si site disorder in ringwoodite if re-ordering occurs rapidly during cooling. Several small VISi peaks in ringwoodite samples may be related to residual defects from this process. In forsterite and wadsleyite, several very small “extra” peaks are observed, many of which are at positions far outside the known range of chemical shifts for $^{29}$Si in silicates. These may be caused by “pseudo-contact” shifts from dipolar interactions with unpaired electron spins on trace impurities of paramagnetic transition metal cations.

Keywords: NMR spectroscopy, forsterite, ringwoodite, wadsleyite, high-pressure studies

INTRODUCTION

The three polymorphs of (Mg,Fe)$_x$SiO$_3$, forsterite, wadsleyite, and ringwoodite (α, β, and γ phases, respectively), are the most abundant minerals in the Earth’s upper mantle and transition zone (Ita and Stixrude 1992). Because ringwoodite has the spinel structure, the possibility of thermally activated tetrahedral-octahedral site disorder, producing significant concentrations of $^\alpha$Si and $^\beta$Mg, has long been suspected, based on ionic radius systematics and thermodynamic considerations (O’Neill and Navrotsky 1984; Hazen et al. 1993; Panero 2008). However, because of the similarity of the X-ray scattering of Si and Mg, direct characterization of the extent of such disorder (defined as x = $^{10}$Mg/$^{12}$Mg$_{tot}$) has been difficult. For example, comparison of tetrahedral cation-oxygen distances in ringwoodite samples synthesized at 20 GPa and 1000 vs. 1400 °C and consideration of typical ionic radii suggested about 2% disorder (4% of Si as $^\gamma$Si) in the latter (Hazen et al. 1993); however, this approach may lead to a significant overestimation (Panero 2008). Nonetheless, recent high-level theoretical calculations have predicted significant disorder in ringwoodite, reaching x values of about 2 to 4% at transition zone temperatures, and highlighting the effects of the resulting point defects on elastic constants as well as inferences of the olivine content in the Earth’s transition zone (Panero 2008).

$^{29}$Si NMR is an ideal approach to directly detecting and quantifying disorder in ringwoodite, as $^{29}$Si has a range of chemical shifts very different than that of $^{28}$Si (Stebbins and Kanzaki 1990; Hazen et al. 1993). Spectra of ringwoodite samples have been reported, but apparently, obtainable signal-to-noise ratios were insufficient to detect $^{28}$Si at predicted concentrations (Ashbrook et al. 2005). Data on wadsleyite and on most other known hydrous and anhydrous, high-pressure Mg silicates have also been reported (Stebbins and Kanzaki 1990; Stebbins 1995; Phillips et al. 1997; Ashbrook et al. 2005; Xue et al. 2008). For this study, we have therefore synthesized forsterite, ringwoodite, and wadsleyite that are highly enriched in $^{28}$Si. The greatly enhanced sensitivity allows us to place accurate constraints on the $^{29}$Si content that can be quenched into ringwoodite. In addition, the extremely high signal-to-noise ratios obtained allowed the detection of several previously unobserved features in the spectra that occur far outside of known chemical shift ranges in silicates. These could be attributable to the effects of unpaired electron spins on trace amounts of impurity ions such as Fe$^{2+}$ and other transition metals.

SAMPLE SYNTHESIS

Most starting materials were synthesized from 99.4% $^{28}$Si-enriched SiO$_2$ (Isonics) and reagent-grade MgO, both dried at 1000 °C. A slight excess of the latter was added to ensure that minor heterogeneities would be unlikely to form $^{28}$Si-bearing phases stable in the pressure range studied (akimotoite, stishovite). Two batches of forsterite were made by grinding reagents together in an agate mortar, then heating for about 7 to 12 days in air at 1500 °C in a Pt crucible with several intermediate grinding steps. One was “doped” with about 0.2 wt% Co$_2$O$_3$ to speed spin-lattice relaxation. After an initial 186 h of heating with three dry grinding steps (Fo-1), this sample was later re-ground in isopropanol to yield finer particle size, then annealed another 100 h (Fo-2). The second $^{28}$Si-enriched batch contained no added Co (Fo-noCo). A third batch was made with reagent-grade amorphous...
silica with natural isotopic abundance and was also undoped (Fo-unen). Electron microprobe (EPMA) analyses confirmed stoichiometry. EPMA detected 0.10 ± 0.02 wt% CoO in the doped forsterite, suggesting some loss during synthesis, and did not detect the most likely other magnetic impurity (FeO and/or Fe₂O₃) at 0.02 wt% level. ICP analysis of the MgO reagent found 10 ± 2 ppm Fe and 8 ± 2 ppm Ni, with other typical magnetic contaminants (e.g., Co, Cr) at <1 ppm. The analysis of the ²⁹SiO₂ provided by the manufacturer indicated 45 ppm Fe, 150 ppm Cu, and 30 ppm Cr.

High-pressure syntheses were done at the Bayerisches Geoinstitut, using the 5000-ton multi-anvil apparatus and unsealed 2 mm diameter Fe foil capsules (Frost et al. 2004). An 18 mm MgO octahedron assembly with a stepped lanthanum chromate heater was used in 54 mm WC cubes with 8 mm corner truncations. Samples were held at temperature for 1.5 h, then quenched by turning off the heater power, cooling to below 500 °C within about 5 s. Two runs were made with the Co-doped forsterite starting material (Fo-1) at nominal pressure and temperature of 21 GPa and 1500 °C. The first yielded a sample that was mostly ringwoodite (RWD), as indicated by powder X-ray diffraction showing only ringwoodite with minor (<5%) wadsleyite, as well as optical microscopy, which is particularly sensitive to non-isotropic phases mixed with cubic ringwoodite. A thermocouple failure in the second apparently led to a somewhat lower temperature (at least 100 °C?) estimated from heater wattage, producing a sample that was mostly wadsleyite (WDS). A third run at 20 GPa and 1300 °C on “Fo-noCo” also resulted in mostly ringwoodite (RWD-noCo). In the high-pressure samples, EPMA analyses detected only Mg₂SiO₄ phases, with means about 0.3 to 0.8 mol% MgO in excess over stoichiometry, presumably from tiny, scattered grains of excess MgO. Measured CoO contents were 0.06 ± 0.02 wt%, with FeO below detection level of 0.02 wt%.

NMR SPECTROSCOPY

²⁹Si NMR spectra were collected with a Varian Inova 400 spectrometer (9.4 T field) at 79.4 MHz, with a Varian/Chemagnetics “T3”-type probe with 3.2 mm zirconia rotors, and are referenced to tetramethylsilane (TMS). Several spectra (not shown) were also collected on a similar spectrometer at 14.1 T field. Small samples (5 mg for the wadsleyite, about 10 mg for the ringwoodite doped samples) were spun at 20 kHz; larger samples (e.g., forsterite, 46 mg) were spun at 12 kHz. One pulse acquisition was used, with pulse lengths of 0.7 μs (30° rf tip angle). A detailed study of relaxation was carried out, using pulse delays ranging from 0.2 to 1800 s (Stebbins et al. in prep). Partially relaxed spectra at relatively short delays (1 to 10 s, up to 60 000 transients) are presented here to highlight fast-relaxing features and/or to enhance signal to noise; however, in no cases were additional phases detected at longer delay times. Five to 20 Hz Gaussian line broadening was applied during data processing. With a 10 s delay, the ringwoodite spectra reach about 50% of their fully relaxed magnetization.

RESULTS AND DISCUSSION

All spectra of the forsterite samples contained only a single, major peak at ~61.8 ± 0.1 ppm, as previously tabulated (Stebbins 1995). Peaks for no other known phases were observed. The full-width at half maximum (FWHM) ranged from 0.2 (undoped samples, Fo-noCo and Fo-unen) to 0.9 ppm (Co-doped, Fo-2). The wadsleyite sample (Fig. 1) contained a single peak at ~78.7 ± 0.1 ppm with FWHM of 0.6 ppm, as well as a minor ringwoodite peak at ~81.3 ± 0.1 ppm (6% of area in relaxed spectra). Both chemical shifts are within uncertainties of previously reported values (Stebbins and Kanzaki 1990; Ashbrook et al. 2005). The Co-doped ringwoodite sample contained about 3.5% wadsleyite, while the Co-free ringwoodite contained about 25% wadsleyite, which relaxed considerably slower. The FWHM for the Co-doped ringwoodite (0.5 ppm) was somewhat broader than for the undoped sample (0.2 ppm). Spectra for both ringwoodite samples contained two small but significant peaks at ~80.1 and ~80.4 ppm, labeled as “X₁” and “X₂” in Figure 1, together making up about 6 ± 2% of the total ²⁹Si signal (independent of relaxation delay). These cannot be assigned to any known Mg silicate, including pyroxenes, majorite, and other high pressure phases (Stebbins 1995; Phillips et al. 1997). The minor peaks are broadened into a single feature in the Co-doped sample. The relative intensities of these peaks are the same in both samples, and they relax at the same rate as the main ringwoodite peak, consistent with (but not proving) their being related to some sort of structural defect sites in the ringwoodite.

The ²⁹Si enrichment enabled very high signal-to-noise ratios to be obtained (e.g., >2000/1 for the ringwoodite and forsterite with pulse delays of 1 s, >400/1 at 300 s), giving great sensitivity to minor spectral features. Figure 2 shows spectra with vertical scales enlarged by about 40× those of Figure 1. Most importantly for the initial goal of this investigation is the lack of detectable signal for VISi in any of these samples. For the ringwoodite, a VISi peak with width comparable to the main ²⁹Si peak would be detected at about the 0.1% level (x = 0.05%); if it were 5× broader (perhaps because of disorder), such a peak would be detectable at the 0.5% level. The detection limits in the smaller wadsleyite sample are about 2× greater, about 0.2 to 1%. This analysis assumes that the signal from VISi, if present, would not relax much more slowly than signals from VISi. Similar relaxation

FIGURE 1. ²⁹Si MAS NMR spectra of wadsleyite (W) and ringwoodite (R) samples (10 s pulse delays). “X₁” and “X₂” mark peaks of unknown origin, possibly disorder-related defect sites in ringwoodite.
rates are indeed typically observed for multiple sites in single-phase silicates when relaxation is dominated by paramagnetic impurities, which is likely to be the case here. For example, the relative intensities of peaks for \(^{29}\text{Si}\), \(^{30}\text{Si}\), and \(^{31}\text{Si}\) in triclinic CaSi\(_2\)O\(_3\) do not depend significantly on pulse delay (Stebbins and Poe 1999); \(^{30}\text{Si}\) and \(^{31}\text{Si}\) peaks in majorite (MgSiO\(_3\)) garnet also relax at similar rates (Phillips et al. 1992). The Co-doped ringwoodite has an additional small peak at –87.5 ppm (area of 0.7%, “X3”), which, like the X1 and X2 peaks, relaxes similarly to the main peak and may again represent some kind of defect, or possibly, an unidentified trace mineral phase.

Octahedrally coordinated Si in ringwoodite is thus not observed at the concentrations of about 2 to 4% of total Si (x = 1 to 2%) expected from theoretical calculations for the synthesis temperatures for the undoped (1300 °C) and Co-doped (1500 °C) samples, respectively (Panero 2008). However, this finding could be consistent with those predications if rapid ordering occurs during cooling. This process is well known to occur in MgAl\(_2\)O\(_4\) spinel, where \(^{29}\text{Mg}\) and \(^{27}\text{Al}\) partially re-order during rapid cooling to temperatures as low as 900 °C (Wood et al. 1986; Redfern et al. 1999). If re-ordering does occur in ringwoodite down to about 1000 °C, then the predicted concentration of \(^{29}\text{Si}\) could fall below our NMR detection limit (Panero 2008). We speculate that imperfect cation re-ordering (i.e., minor residual cation or oxygen displacements from ideal sites) might be responsible for the X1, X2, and/or X3 putative “defect” peaks, but further experimental or theoretical work will be needed to confirm this.

The spectra for the \(^{29}\text{Si}\)-enriched forsterites display an array of small, “extra” peaks, some of which are marked by arrows in Figure 2. Many of these occur at frequencies well outside the known chemical shift range for \(^{29}\text{Si}\) in oxides, having frequencies between –28 and –60 ppm, or in one case, at –128.5 ppm. Unlike the “X” peaks for the ringwoodite, these features relax much faster than the main peaks and are thus enhanced in the spectra shown with short pulse delays of 1 s. Each of the well-resolved “extra” peaks seems to have a roughly similar area, corresponding to about 0.1 to 0.2% of the total, fully relaxed signal. Near to the main peak, multiple “extra” peaks seem to begin to merge into its broadened base. The chemical shifts of these peaks in Fo (in ppm) are identical in several spectra collected at 14.1 T; spinning sidebands were observed for some of the peaks, e.g., that at –207 ppm in Figure 2. To our knowledge, features like these have not been previously described in NMR spectra for silicates.

Ligands other than oxygen can lead to \(^{29}\text{Si}\) chemical shifts outside the range known for oxides: for example, SiC phases at about –20 ppm. However, there is no reason to suspect the presence of significant carbon in these samples, as the reagents contained no significant source of this contaminant and samples were annealed in air at high temperature for many days. Given no other obvious explanation, the likely cause for these “extra” peaks involves the presence of impurity cations that have unpaired electron spins and thus large magnetic moments. The general expectation for such effects is a broadening of resonances and more rapid spin-lattice relaxation, and in fact both effects of the Co\(^{3+}\) dopant were observed for both the forsterite and ringwoodite. Transition metal cations, whose electron spin-lattice relaxation rates enhance their effects on typically observed nuclear spins (Grey et al. 1990), may be especially efficient in “degrading” spectra in this fashion. However, in some cases, measurable shifts in resonant frequencies in solid-state NMR spectra caused by these types of interactions have also been described. For example, large offsets (up to thousands of ppm) have been reported in \(^{119}\text{Sn}\) NMR spectra of rare-earth element stannates with the pyrochlore structure, and were related to through-bond “Fermi contact” (“hyperfine”) interactions (Grey et al. 1989). In some cases, smaller shifts (tens of ppm) caused by more dilute unpaired electron spins at greater distances from the observed nuclide were also seen. These were attributed to a different mechanism involving through-space dipolar couplings between nuclear and unpaired electron spins, the “pseudo-contact shift” (Grey et al. 1989, 1990). This interaction depends on several factors, including on the inverse cube of the distance between the NMR-observed nucleus and the impurity ion with the unpaired electron spin, on the anisotropy in the local electronic environment of the latter, and on the orientation of this anisotropy relative to the vector between the nuclear spin and the latter (Grey et al. 1990). The resulting frequency shift of the NMR resonance can thus be either positive or negative and depends strongly on the structure and the number of magnetic ions in each coordination shell of the NMR-observed atom. For transition metal cations in silicates, it is possible that contact shifts for first neighbor cations are strong enough that resonances are severely shifted and/or broadened; at distances greater than

**Figure 2.** \(^{29}\text{Si}\) MAS NMR spectra of forsterite, wadsleyite, and ringwoodite samples (1 s pulse delays, vertical scales enlarged about 20 to 40× from Fig. 1). Asterisk marks spinning sidebands. Dashed boxes show ranges of known chemical shifts for \(^{29}\text{Si}\) and \(^{31}\text{Si}\) in silicates. Zunyite at –128 ppm is excluded for the unusual structure and composition; as are silicon phosphates that can be as low as –220 ppm (Stebbins 1995). Arrows mark some of the “extra” peaks thought to be related to paramagnetic impurity ions. “X,” marks a peak with a “normal” chemical shift that may represent another defect site in ringwoodite or a minor, unknown, additional phase.
the perhaps third- or fourth-neighbor range, the interaction may drop off to become negligible.

We thus hypothesize that the appearance of the “extra” peaks in the forsterite spectra may be attributed to several factors. The first is the very high sensitivity of the spectra provided by the 20-fold enhancement of the $^{29}$Si abundance. At the same time, the isotopic enrichment means that for a given impurity ion, the probability of it being in the range of distances where it causes a readily observable shift of an NMR resonance is correspondingly greater, i.e., the “sampling” of trace impurities by the NMR signal is much more effective. Secondly, the M sites of the olivine structure, especially M2, have relatively low symmetry, increasing the expected anisotropy at the transition sites. The relatively low symmetry of the overall olivine structure also means that the M cations in a given shell around the Si site are found at a relatively wide range of distances, providing the chance for a variety of observable shifts.

The obvious initial inference was that the Co$^{2+}$ dopant ions caused the “extra” peaks in the forsterite, which led to the synthesis of an undoped second sample. As shown in Figure 2, however, the spectrum of this sample also showed “extra” peaks, at the same positions and relative intensities as in the Co-doped material. It is thus likely that the source of the “extra” peaks is trace levels of other magnetic impurities in the reagents, particularly the Fe and Cr (and the Cu if divalent) reported in the $^{29}$Si silica. This conclusion is supported by comparison of spectra for the Co-doped forsterite after an initial annealing at 1500 °C (Fo-1) with that at the end of a finer grinding and re-annealing step (Fo-2). Both show “extra” peaks of similar intensity, although the peaks in the latter were broader as the Co was diffused throughout more of the forsterite. Again, impurities already dispersed in the reagents are indicated. A spectrum of a synthetic forsterite of natural isotopic abundance and no deliberate doping (Fig. 2) shows hints of some “extra” peaks both below and above the main peak. These are at positions close to some of those in the enriched samples, e.g., –51.8, –56.9, and –66.8 ppm.

The spectrum for the Co-doped ringwoodite sample had a high enough signal to noise ratio to clearly detect the types of “extra,” fast-relaxing peaks as seen for the forsterites. However, no such features were observed (Fig. 2). The smaller size of the wadsleyite sample lead to noisier data, but several such peaks were detected above the noise level, again at positions that cannot be “normal” chemical shifts and that are different from those in the olivine. Although EPMA data suggest that some of the dopant Co may have been lost to the sample containers during high-pressure runs, implying that some other magnetic impurities could also have been extracted, it seems possible that the presence of “extra” peaks in forsterite and wadsleyite, and their absence in ringwoodite, may be attributable to the much higher symmetry of the latter. In the cubic spinel structure, all cations in a given shell around Si are at exactly the same distance, greatly reducing the variety of possible shifts from unpaired electrons. Furthermore, the high symmetry of the likely octahedral sites for the transition metal impurities may reduce the magnitude of the pseudo-contact shift.

The prediction of resonance shifts caused by unpaired electrons requires a detailed description of the properties of the magnetic ions and their site(s) in the structure that are not available for these phases, so that our discussion must remain speculative at this point. Clearly, further NMR (and EPR) studies of silicates with known contents, and structural positions, of paramagnetic impurities will be needed to confirm the peak assignments suggested here. Further studies of this phenomenon in other silicates may provide useful insights not only into the physics of this type of interaction, but possibly into the spatial distribution and order/disorder of minor elements. For example, analysis of contact-shifted $^{17}$O peaks in pyrochlore-structured oxides with mixtures of diamagnetic Y and paramagnetic rare earth cations allowed quantification of the extent of solid solution (Grey et al. 1990).

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