High-Resolution ^{17}O NMR Spectroscopy of Wadsleyite (β-Mg$_2$SiO$_4$)

Sharon E. Ashbrook,[†,⊥] Andrew J. Berry,[‡] William O. Hibberson,[‡] Stefan Steuernagel,[§] and
Stephen Wimperis*,[†]

*School of Chemistry, University of Exeter, Exeter EX4 4QD, United Kingdom, Research School of Earth Sciences,
Australian National University, Canberra ACT 0200, Australia, and Bruker BioSpin GmbH,
76287 Rheinstetten, Germany*

Received June 19, 2003; E-mail: s.wimperis@exeter.ac.uk

(Mg,Fe)$_2$SiO$_4$ is the principal compositional component of the Earth's mantle to a depth of 660 km and transforms from olivine (α) to wadsleyite (β) and, finally, to ringwoodite (γ) with increasing pressure.[1] Wadsleyite, occurring between depths of 410 and ~530 km, has been intensively studied because of its probable relationship to a major seismic discontinuity and its potential as the repository for the largest reservoir of water in the Earth.[1,2] Multiple-quantum (MQ) magic-angle-spinning (MAS)[3] is an established method for obtaining high-resolution ^{17}O NMR spectra of silicates,[4–8] complementing diffraction techniques by, for example, providing indirect information on the structural chemistry of hydrogen. Unfortunately, the method is insensitive and typically requires amounts of ^{17}O-enriched material an order of magnitude greater than can be synthesized at the very high pressures needed to form wadsleyite. Recently, however, with the advent of the satellite-transition (ST) MAS experiment[9] and of very high field magnets,[10] great advances have been made in the sensitivity of high-resolution NMR of quadrupolar nuclei. Here, we report the first ^{17}O NMR study of β-Mg$_2$SiO$_4$ (9.6 mg of 35% ^{17}O-enriched material). Using STMAS at magnetic fields of $B_0 = 9.4$ and 11.7 T and MQMAS at $B_0 = 18.8$ T, we have resolved and assigned all four crystallographically distinct O sites and determined their chemical shift and quadrupolar parameters.

Wadsleyite contains Si$_2$O$_7$ groups that give rise to one approximately trigonal-planar bridging O site (O2), and two distinct tetrahedral O sites (two O3 and four O4).[2,11] There is also an O site (O1) coordinated by five Mg in a distorted square-pyramidal arrangement. The structural, physical, and chemical properties of both wadsleyite and a hydrous form (Mg$_{1.75}$SiH$_{0.5}$O$_4$) have been studied using a variety of techniques, including ^{1}H NMR.[12] High-resolution ^{17}O NMR offers a new and particularly tantalizing prospect as a probe of O-atom coordination which, unlike NMR of other nuclei, can potentially identify the protonated O site in hydrated mantle minerals.

^{17}O-enriched (35%) β-Mg$_2$SiO$_4$ was synthesized from previously prepared α-Mg$_2$SiO$_4$[6] at 16 GPa and 1873 K (1 h) using a MA8-type multiple-anvil apparatus.[13] Approximately 10 mg of wadsleyite was obtained in a single experiment from two sealed cylindrical Pt capsules located on either side of the thermocouple. The total amount of powdered solid filled about $^1/_3$ of a 2.5-mm MAS rotor and was packed on top of an inert spacer to lie in the center of the radio frequency coil.

Figure 1 shows the ^{17}O MAS NMR spectra of wadsleyite recorded at $B_0 = 9.4$, 11.7, and 18.8 T. The spin $I = {}^5/_2$ ^{17}O nucleus possesses a quadrupole moment, and the resonances of the four
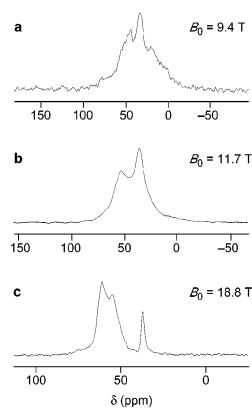
† University of Exeter.
‡ Australian National University.
§ Bruker Biospin GmbH.
⊥ Current address: Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom.

Figure 1. ^{17}O MAS NMR spectra of wadsleyite (β-Mg$_2$SiO$_4$) at magnetic field strengths, B_0, of (a) 9.4 T (2000 acquisitions averaged in 67 min; MAS rate 20 kHz), (b) 11.7 T (20 480 acquisitions averaged in 341 min; MAS rate 25 kHz), and (c) 18.8 T (2048 acquisitions averaged in 34 min; MAS rate 25 kHz). The ppm scales are referenced to H$_2$O.

distinct O sites are thus broadened and shifted by a residual second-order quadrupolar interaction, resulting in a lack of resolution in the MAS spectra.[14] The ^{17}O chemical shift interaction is proportional to B_0, while the second-order quadrupolar interaction is inversely proportional to B_0; hence, the MAS line shapes in Figure 1 depend on B_0 in a complicated fashion. The one fully resolved feature is a narrow resonance at 37 ppm in the $B_0 = 18.8$ T spectrum, evidently corresponding to an ^{17}O nucleus that experiences only a small quadrupolar interaction.

Figure 2 shows the corresponding high-resolution ^{17}O NMR spectra obtained using experimental techniques that refocus the second-order quadrupolar broadening but retain the chemical and quadrupolar shifts. The resonances of the four distinct O sites are resolved in all three two-dimensional spectra as "ridge" line shapes parallel to the δ_2 axis. Sensitivity was a major issue in this study because of the very small amount of material available. The $B_0 = 9.4$ and 11.7 T two-dimensional ^{17}O NMR spectra in Figure 2a and 2b, respectively, were obtained using a phase-modulated split-t_1 STMAS technique.[15] The recently developed STMAS method has attracted much interest because of its relatively high sensitivity,[9,15] but requires that the rotor spinning axis is set to the magic angle (54.736°) with great accuracy (±0.002°) and that very precise synchronization of the spinning period with the t_1 evolution period is used. In contrast, the $B_0 = 18.8$ T two-dimensional ^{17}O NMR spectrum in Figure 2c was obtained using the older (z-filtered[16] triple-quantum) MQMAS technique.[3] At this very high magnetic field strength (i.e., 800 MHz for ^{1}H), the STMAS experiment is more difficult to implement because of the narrower magnet bore and a different NMR probehead design, but the additional sensitivity yielded by the reduction of the second-order quadrupolar broadening with increasing B_0 means that the less sensitive, but technically
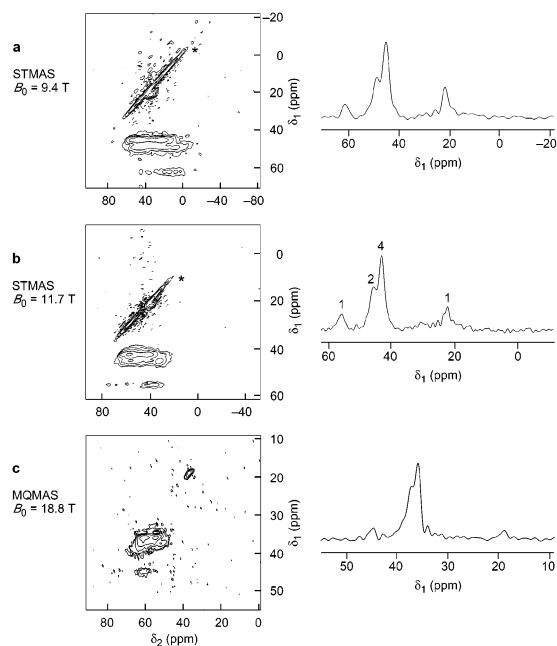
Figure 2. High-resolution two-dimensional and "isotropic" ^{17}O NMR spectra of 9.6 mg of wadsleyite at B_0 fields of (a) 9.4 T (STMAS), (b) 11.7 T (STMAS), and (c) 18.8 T (MQMAS). The uninformative diagonal ridge (marked *) is a characteristic feature of STMAS spectra. The correspondence between the resonance intensities and the 1:2:4:1 relative site populations is indicated in (b). Experimental parameters: (a) 126 560 acquisitions, separated by 2 s, with maximum t_1 period of 7.3 ms, MAS rate 20 kHz; (b) 83 200 acquisitions, separated by 1 s, with maximum t_1 period of 10.3 ms, MAS rate 25 kHz; (c) 240 000 acquisitions, separated by 1 s, with maximum t_1 period of 8.0 ms, MAS rate 25 kHz.

less demanding, MQMAS experiment may be used instead. All of these spectra required considerable total acquisition times: 70 h for Figure 2a, 24 h for Figure 2b, and 67 h for Figure 2c.

The projections of the three two-dimensional ^{17}O NMR spectra onto their δ_1 axes are also shown in Figure 2. These "isotropic" spectra show the presence of the four distinct O sites, with the intensities of the four resonances, 1:2:4:1 in order of decreasing δ_1, reflecting the relative site populations in wadsleyite.

Three methods were used for the extraction of the ^{17}O isotropic chemical shifts (δ_{CS}) and quadrupolar parameters (i.e., the coupling $C_Q = e^2qQ/h$ and asymmetry η, or the composite parameter $P_Q = C_Q\sqrt{(1 + \eta^2/3)}$) from the spectra in Figure 2: (i) the δ_1 and δ_2 shifts of the estimated center-of-gravity of a ridge line shape were used to yield δ_{CS} and P_Q;[6,8,17] (ii) the δ_2 cross section through a ridge line shape was fitted to yield C_Q and η;[6,17] and (iii) the δ_1 shifts at the different B_0 values were used to yield δ_{CS} and P_Q.[18] Method ii was not applied to the narrowest ridge as no second-order broadening was apparent. The three methods yielded a self-consistent set of NMR parameters for the four O sites, and these are given in Table 1, with the small variation across the various methods and spectra providing the error estimates.

The assignment of the four ^{17}O resonances in wadsleyite is straightforward. The relative intensities and site populations indicate that the $\delta_{CS} = 65$ ppm, $P_Q = 3.8$ MHz site is O4 and that the $\delta_{CS} = 66$ ppm, $P_Q = 4.4$ MHz site is O3. These P_Q values are large compared to the values found for nonbridging O sites in less dense

Table 1. ^{17}O Isotropic Chemical Shifts (δ_{CS}), Quadrupolar Products (P_Q), Quadrupolar Couplings (C_Q), Asymmetries (η), Relative Site Populations, and Assignments of the Four O Species in Wadsleyite

δ_{CS} (ppm)	P_Q/MHz	C_Q/MHz	η	relative site population	assignment
76(1)	5.6(1)	4.9(2)	0.9(1)	1	O2
66(1)	4.4(1)	4.4(1)	0.2(1)	2	O3
65(1)	3.8(1)	3.8(1)	0.3(1)	4	O4
38(1)	1.3(1)			1	O1

silicates (typically 2−3 MHz[8,18−20]). The remaining two resonances cannot be assigned from their intensities. However, the large P_Q value[8,18−20] indicates that the $\delta_{CS} = 76$ ppm, $P_Q = 5.6$ MHz site is the Si−O−Si bridging site O2. A graph of δ_{CS} against the mean Si−O bond length for O2, O3, and O4 yields an approximately linear correlation that is in excellent agreement with that found in other magnesium silicates,[8] thereby supporting these three assignments. Finally, the $\delta_{CS} = 38$ ppm, $P_Q = 1.3$ MHz site must be O1, the O atom coordinated by five Mg atoms and not bound to Si. The small P_Q value is consistent with the largely ionic character, and hence relative symmetric electronic environment, of this O atom.

Our results demonstrate that high-resolution ^{17}O NMR studies of milligram quantities of silicate phases can be undertaken using the STMAS technique or a very high B_0 field strength. This opens up the possibility of using ^{17}O NMR to probe high-pressure materials that can only be synthesized in very small quantities. In the case of wadsleyite, we have been able to resolve and assign all four ^{17}O resonances. This work is an essential prerequisite to ^{17}O NMR studies of protonated sites in hydrated phases used as models for mantle water storage.

References

(1) Katsura, T.; Ito, E. *J. Geophys. Res.* **1989**, *94*, 15663.
(2) Smyth, J. R. *Am. Mineral.* **1994**, *79*, 1021.
(3) Frydman, L.; Harwood, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5367.
(4) Stebbins, J. F.; Xu, Z. *Nature* **1997**, *390*, 60.
(5) Dirken, P. J.; Kohn, S. C.; Smith, M. E.; van Eck, E. R. H. *Chem. Phys. Lett.* **1997**, *266*, 568.
(6) Ashbrook, S. E.; Berry, A. J.; Wimperis, S. *Am. Mineral.* **1999**, *84*, 1191.
(7) Stebbins, J. F.; Lee, S. K.; Oglesby, J. V. *Am. Mineral.* **1999**, *84*, 983.
(8) (a) Ashbrook, S. E.; Berry, A. J.; Wimperis, S. *J. Am. Chem. Soc.* **2001**, *123*, 6360. (b) Ashbrook, S. E.; Berry, A. J.; Wimperis, S. *J. Phys. Chem. B* **2002**, *106*, 773.
(9) Gan, Z. *J. Am. Chem. Soc.* **2000**, *122*, 3242.
(10) Gan, Z.; Gor'kov, P.; Cross, T. A.; Samoson, A.; Massiot, D. *J. Am. Chem. Soc.* **2002**, *124*, 5634.
(11) Horiuchi, H.; Sawamoto, H. *Am. Mineral.* **1981**, *66*, 568.
(12) Kohn, S. C.; Brooker, R. A.; Frost, D. J.; Slesinger, A. E.; Wood, B. J. *Am. Mineral.* **2002**, *87*, 293.
(13) Grey, I. E.; Madsen, I. C.; O'Neill, H. St. C.; Kesson, S. E.; Hibberson, W. O. *Neues Jahrb. Mineral., Monatsh.* **1999**, 104.
(14) Ganapathy, S.; Schramm, S.; Oldfield, E. *J. Chem. Phys.* **1982**, *77*, 4360.
(15) Ashbrook, S. E.; Wimperis, S. *J. Magn. Reson.* **2002**, *156*, 269.
(16) Amoureux, J.-P.; Fernandez, C.; Steuernagel, S. *J. Magn. Reson., Ser. A* **1996**, *123*, 116.
(17) Massiot, D.; Touzo, B.; Trumeau, D.; Coutures, J. P.; Virlet, J.; Florian, P.; Grandinetti, P. J. *Solid State Nucl. Magn. Reson.* **1996**, *6*, 73.
(18) Mueller, K. T.; Baltisberger, J. H.; Wooten, E. W.; Pines, A. *J. Phys. Chem.* **1992**, *96*, 7001.
(19) Timken, H. K. C.; Schramm, S. E.; Kirkpatrick, R. J.; Oldfield, E. *J. Phys. Chem.* **1987**, *91*, 1054.
(20) Xue, X.; Stebbins, J. F.; Kanzaki, M. *Am. Mineral.* **1994**, *79*, 31.

JA036777K