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Three- and five-quantum ^{17}O MAS NMR of forsterite Mg_2SiO_4

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ABSTRACT

Three- and five-quantum ^{17}O MAS NMR experiments are used to resolve fully the three crystallographically distinct oxygen species in forsterite (Mg_2SiO_4). The chemical shift and quadrupolar parameters extracted from these spectra are compared with the literature values obtained using conventional ^{17}O MAS and dynamic-angle-spinning (DAS) NMR.

INTRODUCTION

Forsterite (Mg_2SiO_4) is the Mg end-member of the olivine solid solution $Mg_{2-x}Fe_xSiO_4$ and, in its slightly impure form, $Mg_{1.8}Fe_{0.2}SiO_4$, is considered the principal component of the Earth's upper mantle. Forsterite has been studied by ^{17}O NMR (Schramm and Oldfield 1984; Fritsch et al. 1986) and high-resolution spectra of the powdered solid have been obtained by using double rotation (DOR) and dynamic angle spinning (DAS) to remove inhomogeneous second-order quadrupolar broadening (Mueller et al. 1991, 1992). We are using multiple-quantum magic angle spinning (MQMAS) (Frydman and Harwood 1995; Fernandez and Amoureux 1995), a recently developed alternative to DOR and DAS, to resolve crystallographically distinct oxygen species in the ^{17}O NMR spectra of various dense silicates. Several general accounts of MQMAS exist in the literature (Massiot et al. 1996; Brown and Wimperis 1997; Kentgens 1997) and the reader is referred to these for both theoretical and practical details of the basic experiment.

Here, we present the three- and five-quantum ^{17}O MAS NMR spectra of isotopically enriched synthetic forsterite and compare the chemical shift and quadrupolar parameters we obtain with those found using conventional ^{17}O NMR and ^{17}O DAS NMR. Although several three-quantum ^{17}O MAS NMR studies of zeolites and silicate glasses have appeared recently (Dirken et al. 1997; Amoureux et al. 1998; Schaller and Stebbins 1998; Wang and Stebbins 1998; Xu et al. 1998), the present work is a particularly striking illustration of the remarkable site resolution that can be achieved in ^{17}O NMR by three- and five-quantum MAS.

EXPERIMENTAL PROCEDURE

As precursors to the synthesis of ^{17}O-labeled forsterite, MgO and SiO_2 were first synthesized using $H_2{}^{17}O$ (35+%, Cambridge Isotope Laboratories, Inc.). For MgO, the labeled water was added to a stoichiometric amount of Mg_3N_2 in CCl_4, under dry N_2 or Ar, and stirred for several hours. The reaction-moderating CCl_4 was then removed by heating and the resulting $Mg(OH)_2$ powder dehydrated under Ar at 500 °C for 12 hours to give MgO in ~100% yield. For SiO_2, the enriched water was added to excess $SiCl_4$ and refluxed under dry N_2 or Ar for 4 hours. The excess $SiCl_4$ was removed by evaporation and the white solid heated under Ar at 1100 °C for 12 hours to give poorly crystalline SiO_2 in ~66% yield. Finally, stoichiometric amounts of MgO and SiO_2 were mixed, pressed into a pellet, and heated at 1500 °C under N_2 or Ar for 12 hours. The product was analyzed by X-ray diffraction, with several grinding and heating steps required to produce a sample free of impurity phases.

^{17}O NMR experiments were performed at a Larmor frequency of $\nu_0 = 54.2$ MHz on a Bruker MSL 400 spectrometer ($B_0 = 9.4$ T). The forsterite was packed in a 4 mm MAS rotor and spun at ~7.2 kHz. The recycle delay was 1 s. A calibration experiment on H_2O yielded a radiofrequency field strength of $\nu_1 \approx 80$ kHz for the MAS probe used in this work. The conventional ^{17}O MAS NMR spectrum of forsterite (Fig. 1) reveals a composite peak, centered on $\delta \approx 50$ ppm (relative to H_2O), that displays lineshape features characteristic of inhomogeneous second-order quadrupolar broadening. To resolve the distinct oxygen species contributing to this peak, three- and five-quantum ^{17}O MAS NMR spectra (Fig. 2) were recorded using the optimized phase-modu-

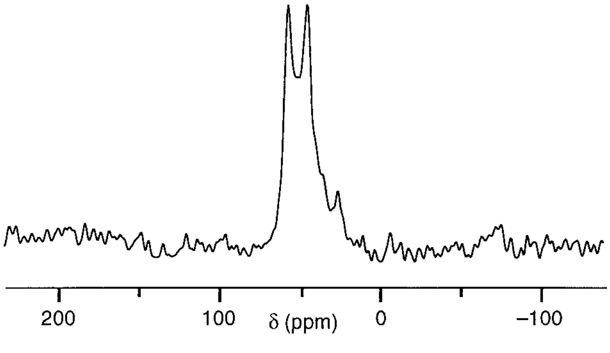

FIGURE 1. Conventional ^{17}O MAS NMR spectrum of forsterite.

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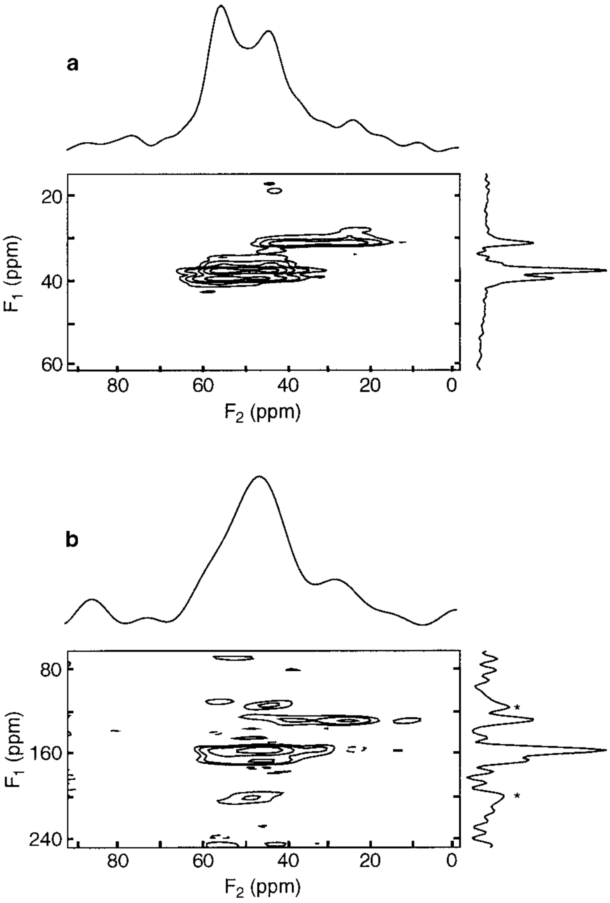

FIGURE 2. (a) Three- and **(b)** five-quantum ^{17}O MAS NMR spectra of forsterite recorded using phase-modulated split-t_1 MQMAS experiments. The displayed F_1 and F_2 spectral widths are **(a)** 2.5 × 5 kHz, extracted from the full 10 × 20 kHz spectrum, and **(b)** 10 × 5 kHz, extracted from the full 50 × 20 kHz spectrum. In **a**, 576 acquisitions were averaged for each of 128 t_1 increments, while in **b**, 2560 acquisitions were averaged for each of 100 t_1 increments. Total experiment times: **(a)** 21 h; **(b)** 71 h. Contour levels: **(a)** 4, 8, 16, 32, and 64%; **(b)** 8, 16, 32, and 64%. Spinning sidebands in the F_1 projection in **b** are marked with an asterisk.

lated split-t_1 MQMAS experiments appropriate for a spin $I = 5/2$ nucleus described in Figure 14b of Brown and Wimperis (1997) and Figure 3 of Brown et al. (1999), respectively.

RESULTS AND DISCUSSION

In each of the two-dimensional spectra (Fig. 2), the three crystallographically distinct oxygen species are resolved by their isotropic chemical and second-order quadrupolar shifts in the F_1 frequency dimension, whereas the second-order broadening of each individual ^{17}O resonance is retained in the F_2 dimension in the form of a "ridge" line shape. Note that, in split-t_1 MQMAS experiments, the second-order broadening is fully refocused at the end of the t_1 evolution period of the two-dimensional experiment and that, as a result, it has not been necessary to apply a shearing transformation to these spectra to obtain solely isotropic shifts in F_1 (Brown and Wimperis 1997). The projections onto the F_2 axes reveal the conventional ^{17}O MAS spectrum of forsterite, somewhat distorted by the multiple-quantum excitation and reconversion processes (especially in Fig. 2b), while, as might be anticipated from the crystal structure (Hazen 1976), the F_1 projections reveal three narrow peaks with intensities approximately in the ratio 1:2:1. Note that, although fully resolved, these three peaks span a F_1 chemical shift range of only ~10 ppm (~540 Hz) in Figure 2a and ~40 ppm (~2200 Hz) in Figure 2b, both corresponding to ~18 ppm in the F_1 frequency scale used by Amoureux and Fernandez (1998).

The F_1 frequency dispersion of the peaks in a five-quantum split-t_1 MAS spectrum of an $I = 5/2$ nucleus is a factor of 155/37 ≈ 4.2 times greater than in the corresponding three-quantum spectrum (Brown et al. 1999). However, this increased dispersion does not translate fully into increased resolution in F_1 because of a concomitant increase in the five-quantum F_1 line width (Amoureux and Fernandez 1998; Brown et al. 1999). Furthermore, as a result of the relative inefficiency of the five-quantum excitation and reconversion pulses, the five-quantum ^{17}O MAS NMR spectrum (Fig. 2b) has a poorer signal-to-noise ratio than the three-quantum spectrum (Fig. 2a). Nevertheless, the five-quantum spectrum is a useful adjunct to the three-quantum results as it provides a second, independent source of ^{17}O chemical shifts and quadrupolar parameters.

The position of the center of gravity of a ridge line shape in the I = 5/2 MQMAS spectra is given by

$$(\delta_1,\delta_2)=\left(\frac{17}{31}\delta_{CS}+\frac{32}{93}\delta_Q,\delta_{CS}-\frac{16}{15}\delta_Q\right) \qquad (1)$$

for the three-quantum split-t_1 spectrum (Brown 1997) and

$$(\delta_1,\delta_2)=\left(\frac{85}{37}\delta_{CS}+\frac{160}{111}\delta_Q,\delta_{CS}-\frac{16}{15}\delta_Q\right) \qquad (2)$$

for the five-quantum split-t_1 spectrum (Brown 1997; Brown et al. 1999). The isotropic chemical shift, δ_{CS}, and isotropic second-order shift parameter, δ_Q, can thus be determined by measuring δ_1 and δ_2, the position of the ridge in the F_1 and F_2 frequency dimensions (Massiot et al. 1996), in either the three- or five-quantum MAS spectrum. The second-order shift parameter δ_Q (in parts per million) is given for a spin $I = 5/2$ nucleus by $\delta_Q = (75\ P_Q/\nu_0)^2$. The "quadrupolar product" (Mueller et al. 1992) P_Q is given by $P_Q = C_Q\sqrt{1+\eta^2/3}$, where $C_Q = e^2qQ/h$ is the quadrupolar coupling constant and η is the asymmetry. The values of δ_{CS} and P_Q extracted in this manner are given in Table 1; uncertainties, given in parentheses, were estimated from a spread of possible δ_1 and δ_2 values.

The separate quadrupolar parameters, C_Q and η, are more informative than the product P_Q and can be extracted directly from MQMAS spectra by fitting the individual inhomogeneously second-order broadened ridge line shapes. Owing to the poorer signal-to-noise ratio in the five-quantum experiment, it was only possible to apply this method to the three-quantum MAS spectrum. The three experimental line shapes and their computer fits are shown in Figure 3, while the C_Q and η values found for the

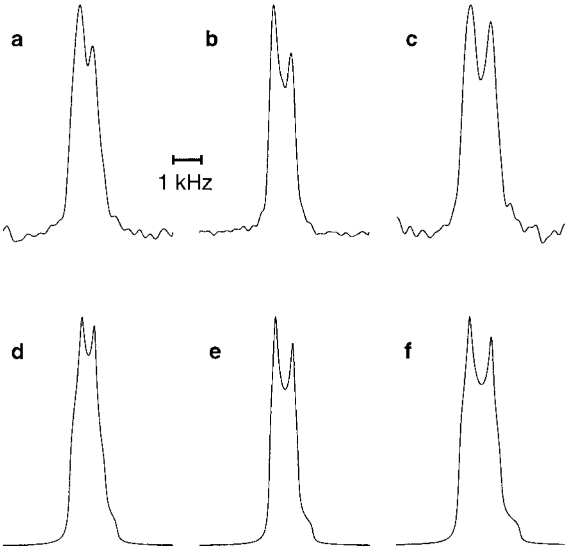

FIGURE 3. **(a, b, c)** Cross sections parallel to the F_2 axis through the three second-order broadened ridge line shapes in the three-quantum ^{17}O MAS NMR spectrum of forsterite (Fig. 2a). The line shapes correspond to those oxygen species with **(a)** δ_{CS} = 64 ppm, **(b)** 61 ppm, and **(c)** 48 ppm. **(d, e, f)** The corresponding computer fits (calculated line shapes), yielding the C_Q and η values given in Table 1. The displayed spectral width is 6 kHz in each case, while all peak heights have been normalized.

three oxygen species are given in Table 1; uncertainties were estimated using a combination of (1) multiple line shape fittings with different starting values and (2) a subjective assessment based on our past experience. As a check for consistency, values of P_Q can be calculated from C_Q and η as 2.6, 2.5, and 2.9 MHz, in good agreement with the P_Q values derived from the three-quantum MAS shift data.

Table 1 compares the results of three previous ^{17}O NMR studies of forsterite (Schramm and Oldfield 1984; Fritsch et al. 1986; Mueller et al. 1992). Using line-shape fitting and assuming the presence of three oxygen species, values of δ_{CS}, C_Q, and η have been extracted from a conventional ^{17}O MAS NMR spectrum (B_0 = 11.7 T). A single-crystal ^{17}O NMR study has yielded values of C_Q and η that agree well with our three-quantum MAS data. Measurements of the δ_1 shifts in DAS spectra recorded at B_0 = 9.4 and 11.7 T have yielded δ_{CS} and P_Q values that accord less well with our data. In this context, however, it may be significant that DAS (also DOR) fails to resolve two of the oxygen species in forsterite at B_0 = 9.4 T (Mueller et al. 1991, 1992).

Table 1 also gives the results of an ab initio calculation of C_Q and η (Winkler et al. 1996). This allows the oxygen species to be identified in order of decreasing δ_{CS} as O2, O3, and O1. This assignment can also be made qualitatively by considering the Si-O-Mg_1/Mg_2/Mg_3 bond angles for each site and the relative site populations (1:1:2 for O1, O2, and O3) (Hazen 1976). The angles for O2 (92°, 92°, 123°) and O3 (90°, 92°, 124°) are similar, defining a highly distorted tetrahedron, but quite different to that of the more symmetrical O1 coordination (118°, 123°, 123°).

TABLE 1. ^{17}O isotropic chemical shifts (δ_{CS}), quadrupolar products (P_Q), quadrupolar coupling constants (C_Q) and asymmetries (η) for the three oxygen species in forsterite (assigned as O2, O3, and O1 in order of decreasing δ_{CS})

Source	δ_{CS} (ppm)	P_Q / MHz	C_Q / MHz	η
Three-quantum MAS (Fig. 2a)	64(1)	2.6(1)	2.5(1)	0.4(1)
	61(1)	2.4(1)	2.5(1)	0.2(1)
	48(1)	2.8(1)	2.9(1)	0.3(1)
Five-quantum MAS (Fig. 2b)	63(1)	3.0(2)	–	–
	61(1)	2.7(1)	–	–
	46(2)	3.1(2)	–	–
Conventional MAS*	62(1)	–	2.35	1.0
	61(1)	–	2.35	0.2
	47(1)	–	2.70	0.3
Single crystal NMR†	–	–	2.53(2)	0.39(1)
	–	–	2.42(2)	0.18(1)
	–	–	2.77(2)	0.28(2)
DAS‡	72(2)	3.3(1)	–	–
	64(2)	2.8(2)	–	–
	49(2)	3.0(2)	–	–
Ab initio calculation§	–	–	2.43	0.44
	–	–	2.29	0.22
	–	–	2.70	0.30

* Schramm and Oldfield (1984).
† Fritsch et al. (1986).
‡ Mueller et al. (1992).
§ Winkler et al. (1996).

Since the C_Q and P_Q values for the three oxygen species are similar, we can assume that the MQMAS peak intensities are approximately quantitative. In this case, the O3 peak is unambiguously identified from the F_1 intensity ratio and, accordingly, the peak of similar δ_{CS} may be assigned to O2.

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REFERENCES CITED

Amoureux, J.P. and Fernandez, C. (1998) Triple-, quintuple- and higher order multiple-quantum MAS NMR of quadrupolar nuclei. Solid State Nuclear Magnetic Resonance, 10, 211–223.

Amoureuz, J.P., Bauer, F., Ernst, H., Fernandez, C., Freude, D., Michel, D., and Pingel, U.T. (1998) ^{17}O multiple-quantum and ^{1}H MAS NMR studies of zeolite ZSM-5. Chemical Physics Letters, 285, 10–14.

Brown, S.P. (1997) Multiple-quantum MAS NMR of half-integer quadrupolar nuclei. D. Phil. thesis, University of Oxford.

Brown, S.P. and Wimperis, S. (1997) Two-dimensional multiple-quantum MAS NMR of quadrupolar nuclei: a comparison of methods. Journal of Magnetic Resonance, 128, 42–61.

Brown, S.P., Ashbrook, S.E., and Wimperis, S. (1999) ^{27}Al multiple-quantum magic angle spinning NMR study of the thermal transformation between the microporous aluminum methylphosphonates AlMePO-β and AlMePO-α. Journal of Physical Chemistry B, 103, 812–817.

Dirken, P.J., Kohn, S.C., Smith, M.E., and van Eck, E.R.H. (1997) Complete resolution of Si-O-Si and Si-O-Al fragments in an aluminosilicate glass by ^{17}O multiple-quantum magic angle spinning NMR spectroscopy. Chemical Physics Letters, 266, 568–574.

Fernandez, C. and Amoureux, J.P. (1995) Two-dimensional multiple-quantum MAS NMR spectroscopy of ^{27}Al in aluminophosphate molecular sieves. Chemical Physics Letters, 242, 449–454.

Fritsch, R., Brinkmann, D., Hafner, S.S., Hosoya, S., Lorberth, J., and Roos, J. (1986) Nuclear quadrupole coupling tensors of ^{17}O in forsterite Mg_2SiO_4. Physics Letters A, 118, 98–102.

Frydman, L. and Harwood, J.S. (1995) Isotropic spectra of half-integer quadrupolar spins from two-dimensional magic angle spinning NMR. Journal of the American Chemical Society, 117, 5367–5368.

Hazen, R.M. (1976) Effects of temperature and pressure on the crystal structure of forsterite. American Mineralogist, 61, 1280–1293.

Kentgens, A.P.M. (1997) A practical guide to solid-state NMR of half-integer quadrupolar nuclei with some applications to disordered systems. Geoderma, 80, 271–306.

Massiot, D., Touzo, B., Trumeau, D., Coutures, J.P., Virlet, J., Florian, P., and Grandinetti, P.J. (1996) Two-dimensional magic angle spinning isotropic reconstruction sequences for quadrupolar nuclei. Solid State Nuclear Magnetic Resonance, 6, 73–83.

Mueller, K.T., Wu, Y., Chmelka, B.F., Stebbins, J., and Pines, A. (1991) High-resolution oxygen-17 NMR of solid silicates. Journal of the American Chemical Society, 113, 32–38.

Mueller, K.T., Baltisberger, J.H., Wooten, E.W., and Pines, A. (1992) Isotropic chemical shifts and quadrupolar parameters for oxygen-17 using dynamic angle spinning NMR. Journal of Physical Chemistry, 96, 7001–7004.

Schaller, T. and Stebbins, J.F. (1998) The structural role of lanthanum and yttrium in aluminosilicate glasses: a ^{27}Al and ^{17}O MAS NMR study. Journal of Physical Chemistry B, 102, 10690–10697.

Schramm, S. and Oldfield, E. (1984) High-resolution oxygen-17 NMR of solids. Journal of the American Chemical Society, 106, 2502–2506.

Wang, S. and Stebbins, J.F. (1998) On the structure of borosilicate glasses: a triple-quantum magic angle spinning ^{17}O nuclear magnetic resonance study. Journal of Non-Crystalline Solids, 231, 286–290.

Winkler, B., Blaha, P., and Schwarz, K. (1996) Ab initio calculation of electric field gradient tensors of forsterite. American Mineralogist, 81, 545–549.

Xu, Z., Maekawa, H., Oglesby, J.V., and Stebbins, J.F. (1998) Oxygen speciation in hydrous silicate glasses: an oxygen-17 NMR study. Journal of the American Chemical Society, 120, 9894–9901.

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