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^{17}O Multiple-Quantum MAS NMR Study of High-Pressure Hydrous Magnesium Silicates

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Abstract: Two ^{17}O-enriched hydrous magnesium silicates, the minerals hydroxyl-chondrodite ($2Mg_2SiO_4.Mg(OH)_2$) and hydroxyl-clinohumite ($4Mg_2SiO_4.Mg(OH)_2$), were synthesized. High-resolution "isotropic" ^{17}O ($I = {}^5/_2$) NMR spectra of the powdered solids were obtained using three- and five-quantum MAS NMR at magnetic field strengths of 9.4 and 16.4 T. These multiple-quantum (MQ) MAS spectra were analyzed to yield the ^{17}O isotropic chemical shifts (δ_{CS}) and quadrupolar parameters (C_Q, η and their "product" P_Q) of the distinct oxygen sites resolved in each sample. The values obtained were compared with those found previously for forsterite (Mg_2SiO_4). The ^{17}O resonances of the protonated (hydroxyl) sites were recorded and assigned with the aid of ^{17}O $\{^1H\}$ cross-polarization and comparison with the spectrum of ^{17}O-enriched brucite ($Mg(OH)_2$). Using all of these data, complete assignments of the five crystallographically inequivalent oxygen sites in hydroxyl-chondrodite and of the nine such sites in hydroxyl-clinohumite are suggested. The validity of these assignments are supported by the observation of a correlation between ^{17}O isotropic chemical shift and Si−O bond length. The ^{29}Si MAS NMR spectra of the two minerals were also obtained.

Introduction

Structural studies of solid silicates have an important role to play in understanding the properties of the Earth's mantle. The dominant mineral in the upper mantle (above a depth of 410 km) is olivine with composition $Mg_{1.8}Fe_{0.2}SiO_4$. A simple model for this is forsterite, Mg_2SiO_4, the Mg end-member of the olivine solid solution $Mg_{2-x}Fe_xSiO_4$. It is estimated that the undepleted or primitive upper mantle contains 200−500 ppm of hydrogen (colloquially termed water).[1,2] Studies of phases in the system $MgO-SiO_2-H_2O$ have determined that all known stoichiometrically hydrous magnesium silicates have only limited stability at upper mantle temperatures and pressures.[3] Nominally anhydrous silicate minerals such as olivine, however, may contain sufficient structurally bound water at defect sites to accommodate the entire mantle water budget.[1,4] The incorporation of water in olivine will affect physical and chemical properties of the mantle such as rheology, convection, conductivity, and partial melting, and also has implications for seismic wave velocities and the evolution of the atmosphere and oceans.

Minerals of the hydroxyl-humite group, $nMg_2SiO_4{\cdot}Mg(OH)_2$ where $n = 1$, 2 (hydroxyl-chondrodite), 3, or 4 (hydroxyl-clinohumite), have been proposed as possible models of the defect sites accommodating water in olivine.[5] These minerals may be viewed as hydrated forms of forsterite and can be described simplistically as comprising n forsterite-like layers alternating with a layer of brucite ($Mg(OH)_2$). Clinohumite-type defects, consisting of randomly distributed brucite-like layers, have been identified in mantle olivines.[5]

The structural chemistry of low levels of nonstoichiometric hydrogen is difficult to determine by diffraction methods and alternative techniques such as IR spectroscopy[6−8] and ^{1}H and ^{29}Si NMR spectroscopy[9−11] have been used to investigate both hydrous and nominally anhydrous silicate minerals. In this paper, we adopt a novel approach and use ^{17}O NMR spectroscopy to study two ^{17}O-enriched hydrous forms of magnesium silicate, the humite group minerals hydroxyl-chondrodite, $2Mg_2SiO_4{\cdot}Mg(OH)_2$, and hydroxyl-clinohumite, $4Mg_2SiO_4{\cdot}Mg(OH)_2$, (hereafter referred to simply as chondrodite and clinohumite) that have been synthesized at high pressure. Our intention is that the present study will serve as a model for future ^{17}O NMR work on ^{17}O-enriched nominally anhydrous minerals that contain nonstoichiometric amounts of water.

The ability of ^{17}O (spin quantum number $I = {}^5/_2$) NMR to yield structural information in powdered solids is usually hindered by the presence of significant second-order quadrupolar broadening of the ^{17}O resonances. The magic angle spinning (MAS) technique, although widely used to improve NMR

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resolution by removing broadening arising from first-order spin interactions, does not fully suppress second-order interactions.[12−14] In consequence, much attention has been focused on the recently developed multiple-quantum magic angle spinning (MQMAS) method,[15] which is able to remove the second-order contribution to the quadrupolar broadening in a two-dimensional experiment, thus yielding high-resolution "isotropic" spectra (i.e., free of any anisotropic or orientationally dependent broadening). The combination of ^{17}O MQMAS NMR[16−20] and the recent application of very high magnetic fields (up to 18.8 T)[21,22] to solid-state NMR promises to be particularly powerful.

The main aims of this paper are: (i) to describe the synthesis of ^{17}O-enriched samples of chondrodite and clinohumite, (ii) to present the results of three- and five-quantum ^{17}O MAS NMR experiments performed at magnetic field strengths of 9.4 and 16.4 T, (iii) to tabulate the ^{17}O isotropic chemical shifts (δ_{CS}) and quadrupolar parameters (C_Q, η, and their "product" P_Q) extracted from the MQMAS spectra and to compare them with values found previously for forsterite, (iv) to use these results and those of additional ^{17}O {^{1}H} cross-polarization experiments on chondrodite, clinohumite and (for comparison) brucite, $Mg(OH)_2$, to suggest complete assignments of the crystallographically inequivalent oxygen sites in the two hydrous silicates, and (v) to test these ^{17}O spectral assignments by examining the possibility of a correlation between the measured NMR parameters and known structural parameters. The ^{29}Si MAS NMR spectra of chondrodite and clinohumite will also be presented.

Experimental Section

Sample Preparation. As precursors to the synthesis of chondrodite and clinohumite, ^{17}O-enriched $Mg(OH)_2$ and SiO_2 were prepared by the addition of $H_2{}^{17}O$ (35+%, Cambridge Isotope Laboratories, Inc.) to Mg_3N_2 (99.6%, Johnson Matthey) and $SiCl_4$ (99.998%, Aldrich).[23] Paramagnetic dopants (sometimes used to increase the spin−lattice relaxation rates) were not added. Synthesis conditions corresponding to the pressure and temperature of the upper mantle were achieved using a 1/2″ (12.7 mm) piston cylinder apparatus with an end-load supplied by a 200 tonne press. Samples were sealed in Pt capsules and surrounded by an assembly consisting of a graphite heater and a NaCl/Pyrex/MgO pressure medium. The experimental conditions were chosen with reference to the pressure−temperature stability field of each phase.[24,25] The products are strongly dependent upon the relative amounts of the reactants and these were adjusted to maximize the yield.

Clinohumite was produced from a 5:2 mixture of $Mg(OH)_2$ and SiO_2 reacted at 35 kbar and 830 °C for 3 h. Around 240 mg of sample was synthesized in two separate experiments. Forsterite (Mg_2SiO_4) was identified by X-ray diffraction as a minor impurity phase; there was no evidence for the presence of brucite ($Mg(OH)_2$). Chondrodite was synthesized at 45 kbar and 900 °C from a stoichiometric mixture of clinohumite and $Mg(OH)_2$. The reaction conditions were maintained for 24 h and 100 mg of chondrodite was produced in a single experiment. This sample also contained a minor amount of brucite.

NMR Experiments. ^{17}O MAS NMR spectra were obtained either at a Larmor frequency of 54.2 MHz on a Bruker MSL 400 spectrometer equipped with a 89 mm bore 9.4 T magnet or at a Larmor frequency of 94.9 MHz on a Bruker DRX 700 spectrometer equipped with a 54 mm bore 16.4 T magnet. Powdered samples were packed inside 4 mm MAS rotors.

We have found that the ^{17}O spin−lattice relaxation rates in chondrodite and clinohumite (and forsterite[23]) appear to be significantly faster than in (for example) chain silicates such as the enstatite minerals. The recycle intervals used in our ^{17}O NMR experiments were optimized experimentally such that the signal intensity was ∼ 30% less than that achieved using the same number of transients with a long recycle interval (∼15 s). A number of "dummy" transients were also acquired. Two-dimensional three-quantum ^{17}O MAS NMR experiments were typically recorded several times with slightly different recycle intervals and no evidence was seen of changes in the relative intensities in the isotropic spectra.

For optimum sensitivity and convenience, two-dimensional three- and five-quantum ^{17}O MAS NMR experiments were performed using "phase-modulated split-t_1" pulse sequences: the three-quantum experiments using the pulse sequence in Figure 14b of ref 26 and the five-quantum using the sequence in Figure 3 of ref 27. Spectra recorded at 9.4 T were obtained with ^{1}H decoupling (radio frequency field strength $\nu_{1H} \approx 77$ kHz), but this was not used in the experiments at 16.4 T. The frequency shifts in all ^{17}O spectra were referenced to H_2O. Further experimental details are either given in the figure legends or discussed in the next section.

Results and Discussion

The structure of forsterite consists of isolated SiO_4 tetrahedra linked by divalent Mg atoms in six-fold coordination, as shown schematically in Figure 1a.[28,29] This results in three inequivalent oxygen species, labeled 1, 2, and 3 in Figure 1a (in accordance with the crystallographic literature), with site populations in the ratio 1:1:2. The humite group minerals, closely related to forsterite, may be described as consisting of n forsterite-like layers alternating with a layer of brucite, $Mg(OH)_2$, with $n = 2$ and 4 for chondrodite and clinohumite, respectively, as shown schematically in Figure 1, b and c.[29−32] Although this description is chemically correct, structurally it is not fully accurate as certain layers of anions are shared between the two components of the structure. The crystal structure in Figure 1b predicts five crystallographically inequivalent oxygen species in chondrodite; four of which are expected to possess an ^{17}O quadrupolar coupling constant, $C_Q = eQV_{zz}/4\pi\epsilon_0 h$, of 2−3 MHz, characteristic of the nonbridging oxygens in the forsterite-like layer,[13,33] and one (labeled 5) expected to have a larger C_Q, perhaps 5−8 MHz,[18] associated with the hydroxyl oxygen. The nuclear quadrupole moment, Q, is a fixed property of any given nuclide and hence these differences between C_Q values reflect differences in the electric field gradient (or, more correctly, the

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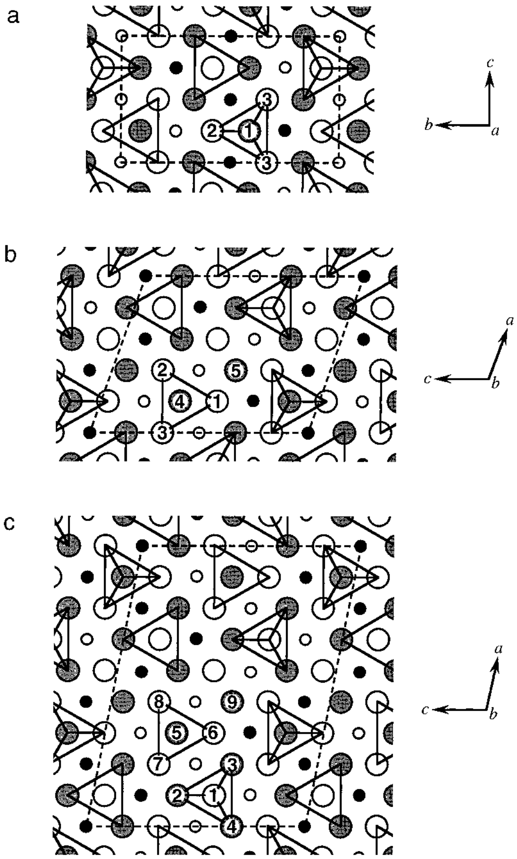

Figure 1. Schematic crystal structures (adapted from ref 29) of (a) forsterite, (b) chondrodite (*P*21/*c*), and (c) clinohumite (*P*21/*c*). Tetrahedra of anions (shown alternately pointing up and down) contain silicon atoms at their centers which are not shown. Oxygen and magnesium atoms are represented by large and small circles, respectively, which are either shaded or unshaded to indicate height in the structure. The unit cell is denoted by dashed lines and crystallographically inequivalent oxygen atoms are numbered in accordance with the crystallographic literature.

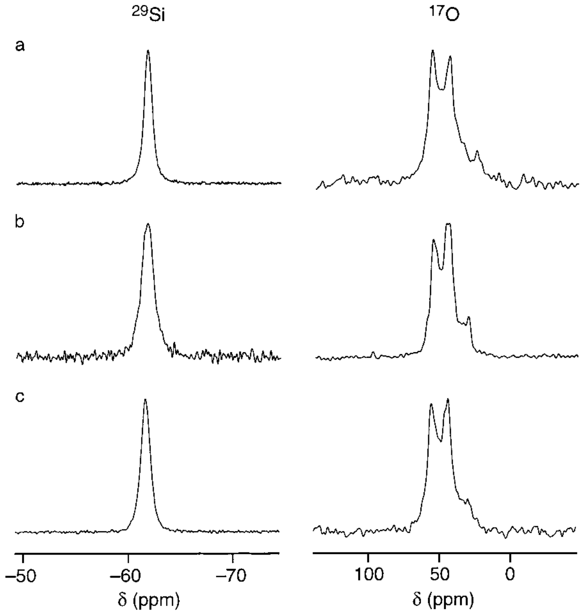

Figure 2. Conventional ^{29}Si (79.5 MHz) and ^{17}O (54.2 MHz) MAS NMR spectra of (a) forsterite, (b) chondrodite, and (c) clinohumite. All ^{29}Si spectra are the result of averaging 160 transients with a 20 s recycle interval. The displayed spectral width is 2 kHz, and the MAS rate was 10 kHz. The ppm scale is referenced to liquid tetramethylsilane. The ^{17}O spectra are the result of averaging (a) 24 transients with a recycle interval of 1 s, (b) 180 transients with a recycle interval of 2 s, and (c) 24 transients with a recycle interval of 2 s. In each case, the displayed spectral width is 10 kHz, and the MAS rate was 7.5 kHz.

dominant principal axis of the electric field gradient tensor), V_{zz}, experienced at each nucleus. For clinohumite, nine inequivalent oxygens are predicted, as shown in Figure 1c; eight nonbridging oxygens and a single hydroxyl oxygen (labeled 9).

The conventional ^{29}Si and ^{17}O MAS NMR spectra of forsterite, chondrodite and clinohumite are shown in Figure 2. Although two inequivalent silicon species are predicted from the structure of clinohumite, the ^{29}Si MAS NMR spectra all display a single sharp resonance at -62 ppm,[34] providing little distinction between the three samples. The ^{17}O MAS NMR spectra all show a complex resonance at ~50 ppm, displaying features characteristic of second-order quadrupolar broadening but comprising overlapping line shapes from more than one crystallographically distinct site. As with ^{29}Si NMR, the ^{17}O MAS spectra of the three materials are remarkably similar, with little indication of the differing number of crystallographically distinct oxygens predicted from the crystal structures in Figure 1.

To resolve the inequivalent oxygen species present the MQMAS technique can be used to remove fully the inhomogeneous second-order quadrupolar broadening, allowing the acquisition of a high-resolution or isotropic ^{17}O NMR spectrum. Figures 3 and 4 show the three- and five-quantum ^{17}O MAS NMR spectra of chondrodite and clinohumite, respectively, recorded at a static magnetic field strength of $B_0 = 9.4$ T. In each spectrum the projection onto the δ_2 axis yields a conventional MAS spectrum, still showing the characteristic features of second-order quadrupolar broadening but distorted by the three- or, in particular, five-quantum excitation and reconversion process. The high-resolution spectrum contained in the projection onto the δ_1 axis consists of narrow, isotropic peaks, that is, peaks free of anisotropic second-order quadrupolar broadening. A complete two-dimensional spectrum thus consists of a series of narrow "ridge" line shapes parallel to the δ_2 axis. Although the δ_1 shift dispersion of the peaks in the five-quantum spectrum is greater than that in the three-quantum spectrum by a factor of ~4.2, this increased dispersion does not translate fully into a resolution increase owing to a corresponding increase in the line width.[35] The lower efficiency of the excitation and reconversion of five-quantum coherences also results in these spectra having a poorer signal-to-noise ratio.

The projections of the chondrodite spectra onto the δ_1 axes in Figure 3 exhibit three distinct oxygen resonances, although closer inspection (particularly of the full two-dimensional spectra) reveals that the more intense central line shape appears to comprise two very closely spaced ridges. The projections of the clinohumite spectra in Figure 4 reveal the existence of five inequivalent oxygen species, with no appreciable increase in resolution obtained in the five-quantum spectrum despite the increase in δ_1 shift dispersion.

The values of the isotropic chemical shift, δ_{CS}, and the quadrupolar product, $P_Q = C_Q\ (1 + \eta^2/3)^{1/2}$, where η, the asymmetry parameter, is defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$, can be obtained from the δ_1 and δ_2 positions of the center of gravity of each ridge line shape.[23,27,36] Specifically, it can be shown that, for the $I = {}^5\!/_2$ three-quantum split-t_1 MAS spectra in

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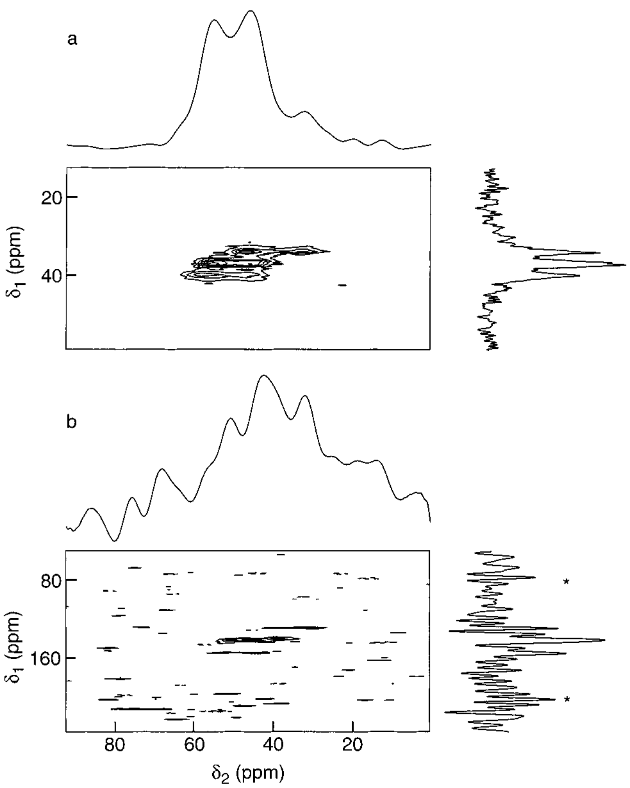

Figure 3. (a) Three- and (b) five-quantum ^{17}O (54.2 MHz) MAS NMR spectra of chondrodite recorded using phase-modulated split-t_1 experiments. In (a) 480 transients were averaged for each of 256 t_1 increments of 250 μs with a recycle interval of 2 s, while in (b) 1600 transients were averaged for each of 192 t_1 increments of 62.5 μs with a recycle interval of 1 s. Contour levels are drawn at (a) 15, 30, 45, 60, 75, and 90% and (b) 50, 70, and 90% of the maximum value. The MAS rate was 7.5 kHz. Spinning sidebands in the δ_1 projections are marked with an asterisk.

Figures 3a and 4a,

$$\delta_{CS} = \frac{31\delta_1 + 10\delta_2}{27} \tag{1a}$$

$$P_Q = \sqrt{\frac{\nu_0^2(31\delta_1 - 17\delta_2)}{162000}} \tag{1b}$$

while for the $I = {}^5/_2$ five-quantum split-t_1 MAS spectra in Figures 3b and 4b,

$$\delta_{CS} = \frac{37\delta_1 + 50\delta_2}{135} \tag{2a}$$

$$P_Q = \sqrt{\frac{\nu_0^2(37\delta_1 - 85\delta_2)}{810000}} \tag{2b}$$

where δ_1 and δ_2 are ppm values and ν_0 is the Larmor frequency in Hz. The values obtained are shown in Table 1, together with those found in a previous ^{17}O MQMAS study of forsterite.[23] The separate quadrupolar parameters C_Q and η (as opposed to the composite parameter P_Q) may be extracted directly from the MQMAS spectra by fitting the inhomogeneously broadened second-order line shapes that result from taking cross-sections through the two-dimensional ridges parallel to the δ_2 axis.[23,36]

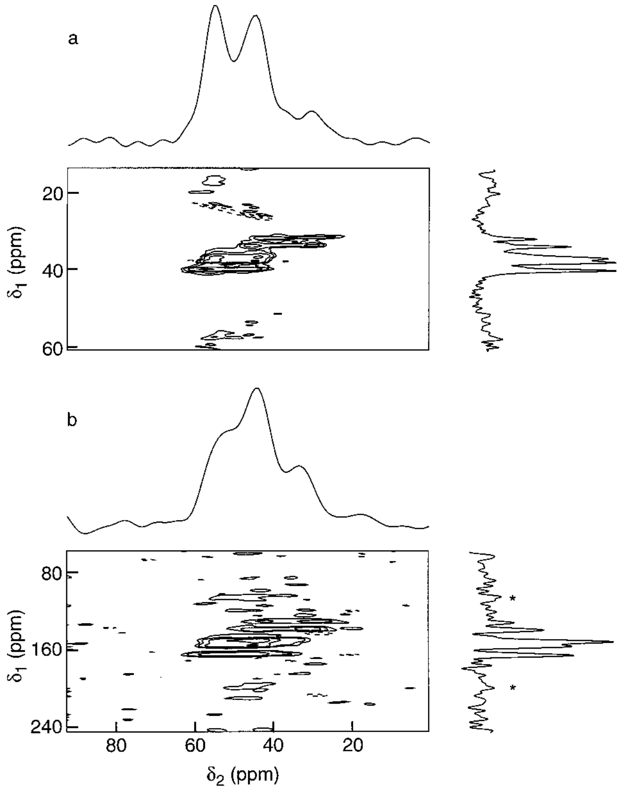

Figure 4. (a) Three- and (b) five-quantum ^{17}O (54.2 MHz) MAS NMR spectra of clinohumite recorded using phase-modulated split-t_1 experiments. In (a) 2208 transients were averaged for each of 96 t_1 increments of 250 μs with a recycle interval of 1.5 s, while in (b) 2400 transients were averaged for each of 64 t_1 increments of 62.5 μs with a recycle interval of 1.5 s. Contour levels are drawn at 8, 16, 32, and 64% of the maximum value. In each case, the MAS rate was 7.6 kHz. Spinning sidebands in the δ_1 projections are marked with an asterisk.

Owing to the poorer signal-to-noise ratio in the five-quantum results, this method was applied only to the three-quantum spectra in Figures 3a and 4a and the resulting values of C_Q and η are also given in Table 1. The uncertainties in the C_Q and η values were obtained from a combination of multiple line shape fittings with different initial conditions and a subjective assessment of the error involved, based on previous experience. The P_Q, C_Q, and η values given in Table 1 are all in good mutual agreement.

The P_Q values displayed in Table 1, between 2.3 and 2.7 MHz for chondrodite and clinohumite, are characteristic of oxygen atoms in nonbridging sites,[13,33] indicating that the hydroxyl oxygens, expected to possess a P_Q value around 5−8 MHz,[18] are not present in Figures 3 and 4. The spectra of chondrodite (Figure 3) appear to contain four distinct nonbridging oxygen species, two of which are only barely resolved in δ_1, corresponding to the four inequivalent oxygen sites shown in Figure 1b. However, the spectra of clinohumite display only five peaks instead of the eight expected from the crystal structure. The approximate ratio of the resonance intensities in the isotropic spectrum (2:2:2:1:1 in order of decreasing δ_1) suggests that all eight inequivalent nonbridging oxygens are observed, but that some of the sites are not resolved, occurring as doubly intense resonances. Although MQMAS is not generally a quantitative technique, owing to the strong dependence of the efficiency of multiple-quantum excitation and reconversion on the magnitude of the quadrupolar interaction, it is possible in this case to interpret the intensity ratios due to the very similar P_Q values of the sites.

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Table 1. ^{17}O Isotropic Chemical Shifts (δ_{CS}), Quadrupolar Products (P_{Q}), Quadrupolar Coupling Constants (C_{Q}), Asymmetries (η), and Tentative Assignments of the Non-bridging Oxygen Species in Forsterite, Chondrodite, and Clinohumite

mineral (spectrum)	δ_{CS} (ppm)	P_{Q}/MHz	C_{Q}/MHz	η	assignment
forsterite	64(1)	2.6(1)	2.5(1)	0.4(1)	O2
three-quantum	61(1)	2.4(1)	2.5(1)	0.2(1)	O3
MAS (ref 23)	48(1)	2.8(1)	2.9(1)	0.3(1)	O1
chondrodite	63(1)	2.6(1)	2.5(1)	0.3(1)	O1
three-quantum	60(2)	2.3(2)	2.3(1)	0.2(1)	O3
MAS (54.2 MHz)	59(2)	2.3(2)	2.3(1)	0.3(1)	O2
(Figure 3a)	52(1)	2.7(1)	2.7(1)	0.2(1)	O4
chondrodite	63(2)	2.7(2)	–	–	O1
five-quantum	60(2)	2.4(2)	–	–	O3
MAS (54.2 MHz)	58(2)	2.4(2)	–	–	O2
(Figure 3b)	51(2)	2.6(2)	–	–	O4
clinohumite	64(1)	2.5(2)	2.5(1)	0.3(1)	O2 + O6
three-quantum	61(1)	2.4(2)	2.4(1)	0.2(1)	O3 + O4
MAS (54.2 MHz)	60(1)	2.4(1)	2.4(1)	0.3(1)	O7 + O8
(Figure 4a)	52(1)	2.7(1)	2.8(1)	0.2(1)	O5
	49(1)	2.7(1)	2.7(1)	0.3(1)	O1
clinohumite	64(1)	2.6(2)	–	–	O2 + O6
five-quantum	61(1)	2.3(2)	–	–	O3 + O4
MAS (54.2 MHz)	58(1)	2.5(1)	–	–	O7 + O8
(Figure 4b)	53(1)	2.6(1)	–	–	O5
	50(1)	2.6(1)	–	–	O1
clinohumite	65(1)	2.5(1)	2.5(2)	0.3(1)	O2
three-quantum	64(1)	2.5(1)	2.4(1)	0.2(1)	O6
MAS (94.9 MHz)	61(2)	2.3(2)	2.3(1)	0.1(1)	O3 + O4
(Figure 7)	60(2)	2.3(2)	2.4(1)	0.2(1)	O7
	59(2)	2.4(2)	2.4(1)	0.2(1)	O8
	52(1)	2.7(1)	2.7(2)	0.2(2)	O5
	49(1)	2.7(1)	2.7(1)	0.2(1)	O1

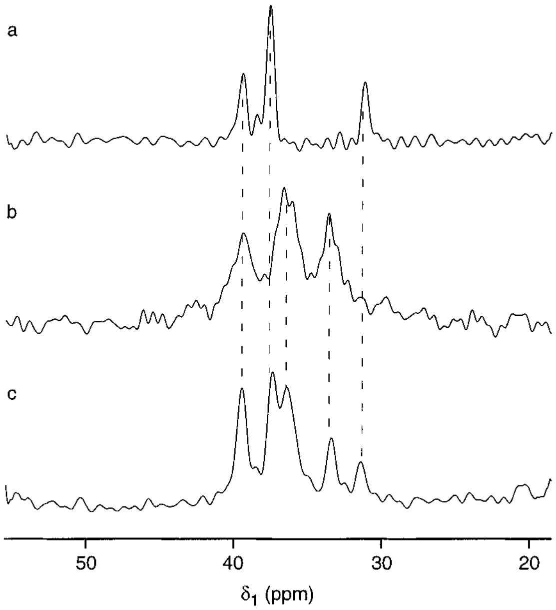

Figure 5. Isotropic projections of three-quantum ^{17}O (54.2 MHz) MAS NMR spectra of (a) forsterite, (b) chondrodite, and (c) clinohumite recorded using phase-modulated split-t_1 experiments. In (a) and (c) 480 transients were averaged for each of 96 t_1 increments of 250 μs with a recycle interval of 1 s. The MAS rate in (a) and (c) was 7.6 kHz. The projection in (b) is that shown in Figure 3a. The vertical dashed lines are intended to facilitate comparison of these projections.

Without confirmation from ab initio calculations of C_{Q} and η (as was possible for forsterite[37]), a complete assignment of the resonances observed in the multiple-quantum MAS spectra of chondrodite and clinohumite is expected to be tentative only. However, a consideration of the isotropic spectra of all three compounds as shown in Figure 5 does enable such an assignment to be made. The resonances in the isotropic spectrum of forsterite (Figure 5a) have been assigned as O2, O3, and O1 in order of decreasing ppm.[23] Descending the humite series to chondrodite (Figure 5b), it can be seen that the isotropic spectrum contains four resonances. The structures of chondrodite and forsterite are quite similar and it is not surprising that the general forms of the two spectra are also similar. This allows correlation of peaks in the assigned forsterite spectrum to unassigned chondrodite resonances. The two closely spaced resonances with a δ_1 frequency of ~36.5 ppm can be assigned as O2 and O3 (Figure 1b), slightly shifted from the position of the doubly degenerate O3 resonance observed in forsterite and no longer identical owing to the reduced symmetry. The resonance with the highest δ_1 shift (~39.5 ppm) in Figure 5b may be assigned as O1, owing to its presence in the spectra of both forsterite and chondrodite. The Si–O–Mg1/Mg2/Mg3 bond angles for this oxygen species (91°, 90°, 123°) are similar to those observed for O2 and O3. The remaining site is assigned to O4. The chemical shift of this species ($\delta_{\mathrm{CS}} = 52$ ppm) is quite distinct from those assigned as O1, O2 and O3 ($\delta_{\mathrm{CS}} =$ 59–63 ppm) and it is noted that the Si–O–Mg1/Mg2/Mg3 bond angles for O4 (120°, 121°, 121°) are significantly different from those found for the other nonbridging oxygen species in chondrodite.

A noticeable feature of the projections in Figure 5 is the resemblance of the isotropic spectrum of clinohumite to the sum of the forsterite and chondrodite spectra. This observation may be rationalized at a simplistic level by noting that the crystal structure of clinohumite (Figure 1c) comprises both chondrodite-like (O5–O8) and forsterite-like (O1–O4) blocks in equal proportions. Therefore, it is possible to assign tentatively the five distinct resonances displayed in clinohumite. The resonances with the lower δ_1 shifts (~31.0 and ~33.5 ppm), may be assigned as O1 and O5, respectively, on the basis of their intensities and their relation to similar peaks in Figure 5, a and b. The resonance with the highest δ_1 shift (~39.5 ppm), may be assigned as a combination of O2 and O6, with peaks in identical positions obtained in the isotropic spectra of both forsterite and chondrodite. Similarly, the intensities and relation to the spectra of forsterite and chondrodite would suggest that the resonances with δ_1 shifts of ~37.5 and ~36.5 ppm correspond to a combination of O3 and O4 and a combination of O7 and O8, respectively. Owing to the lower symmetry of clinohumite, the two sites corresponding to O3 in forsterite are no longer crystallographically identical (O3 and O4), although they might be expected to possess very similar environments.

The assignments of the forsterite, chondrodite and clinohumite ^{17}O NMR spectra suggested here and in ref 23 can be tested by examining whether the measured NMR parameters correlate with known structural parameters. A number of previous studies have found a correlation between chemical shift and Si–O–Si bond angles in bridging oxygens,[38–40] although no such correlation was found in a more recent investigation.[41] By contrast, for the nonbridging oxygens studied in this work, Figure 6 shows that, using the assignments in Table 1 of the 54.2 MHz three-quantum MAS data, there appears to be an approximately linear

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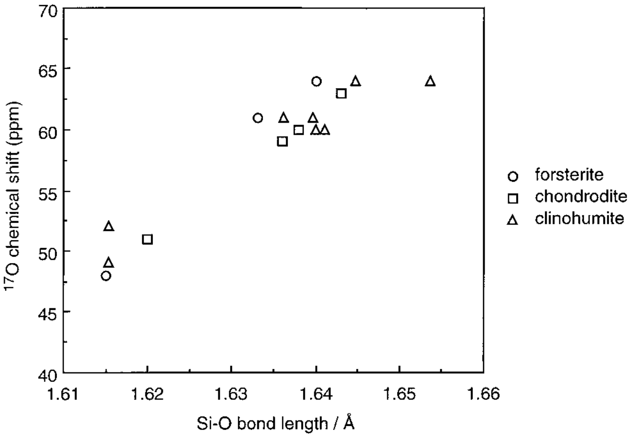

Figure 6. Plot of ^{17}O isotropic chemical shifts (δ_{CS}) versus Si−O equilibrium bond length. The tentative assignments of the ^{17}O (54.2 MHz) three-quantum MAS NMR spectra of forsterite, chondrodite, and clinohumite given in Table 1 have been used.

correlation between ^{17}O isotropic chemical shift and Si−O bond length,[28,30−32,42] with regression analysis yielding $d(\delta_{CS})/dr_{Si-O} = +440$ ppm/Å ($R^2 = 0.897$).

Both the sign and order of magnitude of the gradient observed in Figure 6 are in general agreement with ab initio calculations of changes in chemical shielding upon covalent bond extension in a wide range of small molecules.[43,44] However, to confirm this correlation for the specific example of an isolated SiO_4^{4-} group, quantum-mechanical (distributed gauge) calculations were performed using the CTOCD-PZ2 option of the SYSMO package,[45] with a 6-311++G (3df, 3pd) basis set for the silicon and a 6-31G* basis set for the oxygen atoms. For a perfectly tetrahedral anion with all four Si−O bond lengths equal to 1.634 Å (the mean value across forsterite, chondrodite and clinohumite), the absolute ^{17}O isotropic chemical shielding, σ_{iso}, was calculated as 182 ppm. The chemical shift gradient calculated with respect to variation of one of the four Si−O bond lengths was $d(\delta_{CS})/dr_{Si-O} = +1200$ ppm/Å, concurring with the sign of the gradient observed in Figure 6 and hence, by extension, supporting the empirical ^{17}O resonance assignments upon which Figure 6 is based. The magnitude of the calculated gradient is greater than that found experimentally but such overestimation is to be anticipated in view of the modest basis, small size, and high charge of the structural fragment used in the calculation.

Figure 7 shows a three-quantum ^{17}O MAS NMR spectrum of clinohumite recorded at $B_0 = 16.4$ T. The values of δ_{CS} and P_Q obtained from the δ_1 and δ_2 positions of the center of gravity of each ridge line shape are shown in Table 1. The increased chemical shift dispersion afforded by the higher B_0 field strength has resulted in a splitting of the resonance now at $\delta_1 \approx 33$ ppm and a distinct shoulder on the resonance with the highest δ_1 shift. Therefore, the predictions based upon the intensity ratios observed in Figure 4 are supported. However, no splitting is observed in the resonance with an δ_1 shift of ~34 ppm, assigned above to a combination of O3 and O4, confirming the very similar nature of these oxygen species.

The ^{17}O MAS and MQMAS spectra of chondrodite and clinohumite shown in Figures 2, 3, 4, and 5 provide no evidence for sites with C_Q values characteristic of an OH oxygen. To investigate the nature of such an oxygen environment, ^{17}O isotopically enriched brucite ($Mg(OH)_2$) was used as a model. The environment of the OH oxygen nuclei in brucite is broadly similar to those in clinohumite and chondrodite (tetrahedral coordination by three magnesiums and one hydrogen), and it is likely that their ^{17}O quadrupolar interaction and isotropic chemical shift will closely match those in the other two minerals. The conventional ^{17}O NMR spectrum of a static sample of brucite (Figure 8a) exhibits a second-order quadrupolar broadened line shape that, when fitted, yields $C_Q = 6.8$ MHz, $\eta = 0$, and $\delta_{CS} = 25$ ppm.[46] It should be noted that, owing to the large quadrupolar interaction, it is not possible to obtain a recognizable MAS spectrum of brucite at the spinning rates and magnetic field strengths used in Figures 3 and 4 ($\nu_R \leq 10$ kHz and $B_0 = 9.4$ T). Owing to the spatial proximity of the nuclei, ^{17}O {^1H} cross-polarization yields the enhanced brucite spectrum shown in Figure 8b.[46,47]

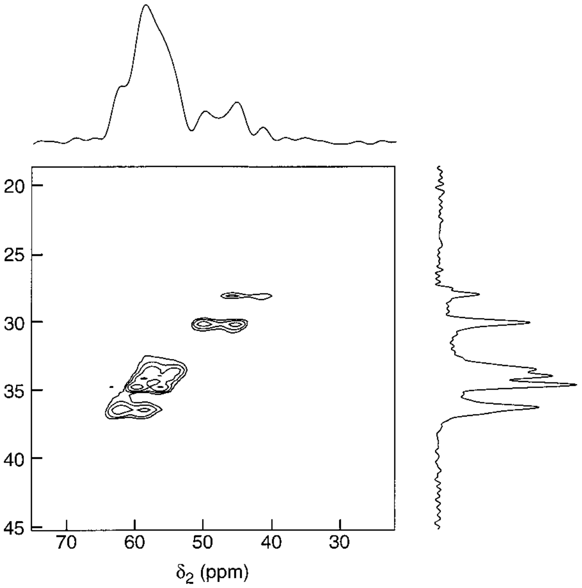

Figure 7. Three-quantum ^{17}O (94.9 MHz) MAS NMR spectrum of clinohumite recorded using a phase-modulated split-t_1 experiment. The spectrum is the result of averaging 96 transients for each of 574 t_1 increments of 50 μs with a recycle interval of 0.7 s. Contour levels are drawn at 8, 16, 32, and 64% of the maximum value. The MAS rate was 12 kHz.

The ^{17}O NMR spectra of static samples of chondrodite and clinohumite are shown in Figure 8, c and e, respectively. Each spectrum displays a composite line shape, showing both a narrow feature and a broader component typical of an oxygen environment with a much larger quadrupolar interaction. Cross-polarized spectra of static samples of chondrodite and clinohumite, recorded using experimental parameters determined from the cross-polarization of brucite, are shown in Figure 8, d and f. In each case, the narrow feature is no longer present, indicating that it derives from the forsterite-like layers which do not contain ^1H, while the broader signal remains, allowing its assignment to the hydroxyl oxygen species.

The values of C_Q, η, and δ_{CS}, extracted from a fitting of the spectra in Figure 8, d and f, are given in Table 2. It can be seen that the hydroxyl oxygens in chondrodite possess a slightly smaller quadrupolar coupling constant than those in clinohumite, with both appearing to be very similar to that found in brucite. The magnitude of the quadrupolar interaction for both com-

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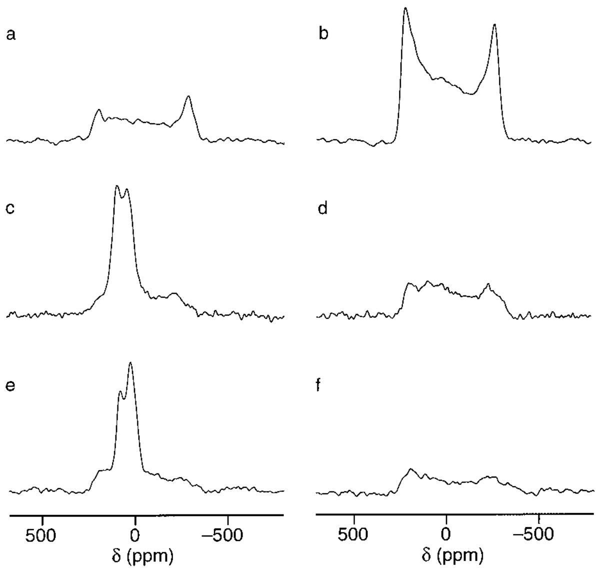

Figure 8. (a) Conventional and (b) cross-polarized ^{17}O (54.2 MHz) NMR spectra of brucite: 1200 transients averaged with a 2 s recycle interval. (c) Conventional and (d) cross-polarized ^{17}O (54.2 MHz) NMR spectra of chondrodite: 3200 transients averaged with a 2 s recycle interval. (e) Conventional and (f) cross-polarized ^{17}O (54.2 MHz) NMR spectra of clinohumite: 14400 transients averaged with a 1 s recycle interval. Cross-polarization was performed with a ^{17}O radio frequency field strength of $\nu_{1S} \approx 25$ kHz, a ^{1}H field strength of $\nu_{1I} \approx 77$ kHz, and a spin-locking duration of (b) 0.4 ms, (d) 2 ms, and (f) 0.5 ms. Spin−echoes (formed by selective 180° pulses) were used to acquire the spectra of these static samples.

Table 2. ^{17}O Isotropic Chemical Shifts (δ_{CS}), Quadrupolar Coupling Constants (C_Q), and Asymmetries (η) for the Hydroxyl Oxygen Species in Brucite, Chondrodite (O5), and Clinohumite (O9)

mineral (spectrum)	δ_{CS} (ppm)	C_Q/MHz	η
Brucite (Figure 8a)	25(1)	6.8(1)	0.0(1)
Chondrodite (Figure 8d)	25(3)	6.6(1)	0.1(2)
Clinohumite (Figure 8f)	25(3)	7.0(1)	0.2(2)

pounds is responsible for the nonappearance of this resonance in the ^{17}O MAS spectra in Figure 2. However, the conventional ^{17}O MAS NMR spectrum of clinohumite, recorded at $B_0 = 16.4$ T and shown in Figure 9, displays both the narrow resonances of the nonbridging oxygen species and a broader signal at lower frequency ($\delta \approx -5$ ppm) ascribed to the hydroxyl oxygen. The reduction in quadrupolar broadening achieved at the higher static field strength has allowed the observation of the protonated oxygen signal under MAS conditions.

Conclusions

The humite minerals chondrodite and clinohumite, proposed as possible models for the site of water incorporation into the forsterite structure, were synthesized under high-pressure conditions and studied using both two-dimensional three- and five-quantum ^{17}O MAS NMR techniques. The resulting spectra were analyzed to obtain values of δ_{CS}, P_Q, C_Q, and η. The great potential of ^{17}O MQMAS to resolve the many crystallographically distinct oxygen species, all of which overlap considerably in the MAS spectra, was demonstrated and tentative assignments of the spectra were achieved. It is the quality of the data provided by ^{17}O MQMAS NMR, particularly at high magnetic field strengths, that makes these assignments possible, and it is interesting to note, despite the extensive work carried out on ^{17}O-enriched minerals using the dynamic angle spinning (DAS) and double rotation (DOR) techniques,[48−50] that the current work appears to represent the first time that assignments of such complex ^{17}O NMR spectra have been attempted. Cross-polarization was also used to "edit" the ^{17}O spectra of chondrodite and clinohumite to allow the selective observation of the hydroxyl oxygens, thereby confirming that ^{17}O NMR has allowed the identification of all inequivalent oxygen species in these samples.

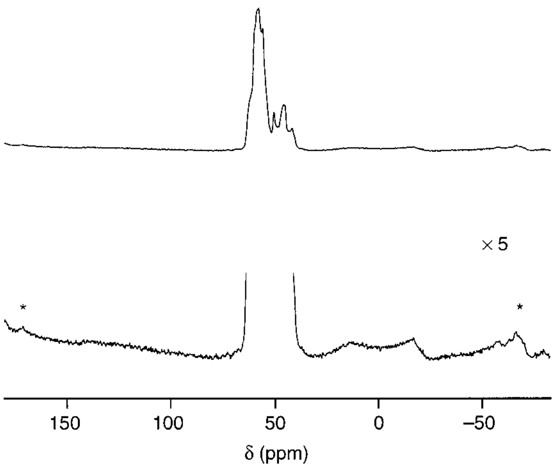

Figure 9. ^{17}O (94.9 MHz) MAS NMR spectrum of clinohumite: 256 transients averaged with a recycle interval of 1 s. The lower trace is shown with an expanded vertical scale. The MAS rate was 12 kHz. Spinning sidebands are marked with an asterisk.

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