

Crystal structure of monoclinic hydrous wadsleyite [β -(Mg,Fe) $_2$ SiO $_4$]

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ABSTRACT

Wadsleyite [β -(Mg,Fe) $_2$ SiO $_4$] is known to accept variable amounts of H and may be an important reservoir of H in the transition zone of the mantle. The crystal structure of Fo $_{94.6}$ hydrous wadsleyite (Mg $_{1.730}$ Fe $_{0.098}$ Al $_{0.008}$ Si $_{10.991}$ H $_{0.355}$ O $_4$) synthesized at 1400 °C and 17 GPa was refined in space group *I2/m* from 1784 measured intensities of which 830 were unique, and, of these, 650 were of intensity greater than 4 σ . Unit cell parameters are $a = 5.6715(7)$, $b = 11.582(2)$, $c = 8.258(1)$ Å, and $\beta = 90.397(9)^\circ$. The final $R(F)$ for all reflections was 0.026 ($R_w = 0.024$); goodness of fit was 1.68. An H position was located on the nonsilicate O atom (O1). Partial occupancy of a normally vacant tetrahedral site adjacent to M3 was observed. This is postulated to be the result of Si moving from M3 to the adjacent tetrahedral void on decompression. Deviation from orthorhombic symmetry appears to result from ordering of H, (Mg, Fe), and possibly Si, within the two nonequivalent M3 sites.

INTRODUCTION

The presence of H in rocks has a major effect on melting temperature, strength, and elastic properties and thus may control melt generation, solid state convection, and seismic velocities in the Earth. Also, the incorporation of even minor amounts of H in mantle phases may have played a central role in the development and evolution of Earth's hydrosphere. One tenth of one percent H $_2$ O by weight in the minerals of the transition zone (400–670 km depth) is an amount equal to 800 m of liquid water over the surface of the planet.

The stabilities of possible hydrous and anhydrous phases under upper mantle conditions have been reviewed by Thompson (1992). Numerous hydrous high pressure magnesium silicate phases have now been characterized. Phase A [2Mg $_2$ SiO $_4$ ·3Mg(OH) $_2$] is a high-Mg phase synthesized at the relatively low temperature of 800 °C at 7.7 GPa (Horiuchi et al. 1979). Finger et al. (1991) reported the crystal structures of phase B [Mg $_{12}$ Si $_4$ O $_{19}$ (OH) $_2$] and anhydrous phase B (Mg $_{14}$ Si $_5$ O $_{24}$). Pacalo and Parise (1992) reported a superhydrous modification of phase B [Mg $_{10}$ Si $_3$ O $_{14}$ (OH) $_4$]. Phase A, phase B, and superhydrous B all have Mg/Si ratios greater than 2.0. Phase E (Mg $_{2.08}$ Si $_{1.16}$ H $_{3.2}$ O $_6$) synthesized at 15 GPa and 1000 °C has an Mg/Si ratio close to that of forsterite but has a low density of 2.822 g/cm 3 (Kudoh et al. 1993). Phase F (Mg $_{3.35}$ Si $_{5.51}$ H $_{7.26}$ O $_{18}$) synthesized at 17 GPa and 1000 °C has an Mg/Si ratio less than 1.0 and also has a low density of 2.826 g/cm 3 (Kudoh et al. 1995). In addition to these stoichiometrically hydrous phases, Bell and Rossman (1992) and Pawley et al. (1993) showed

that nominally anhydrous phases may contain very significant amounts of hydrogen and thus may serve as major sinks for protons in the mantle.

Among phases stable in the transition zone, nominally anhydrous wadsleyite (β -Mg $_2$ SiO $_4$) might serve as a host phase for H, since it contains an O site not bonded to Si with an anomalously shallow electrostatic potential (Smyth 1987, 1994). Downs (1989) predicted that the bridging O might be a better site for protonation, although protonation of bridging O atoms is unknown among stoichiometric silicates. Wright and Catlow (1996) calculated the energetics of H substitution in wadsleyite and favored protonation of the nonsilicate O. McMillan et al. (1991) observed a small amount of OH in wadsleyite synthesized under nearly anhydrous conditions. Young et al. (1993) and Gasparik (1993) observed major amounts of OH in Fo $_{92}$ wadsleyite with up to 1.6% of all O atoms protonated. Theoretical studies predicted that the phase may contain up to 3.3 wt% H $_2$ O (Smyth 1987, 1994). Inoue et al. (1995) synthesized Fo $_{100}$ wadsleyite with 3.3 wt% H $_2$ O, and Kudoh et al. (1996) determined the structure of one of these samples of orthorhombic hydrous wadsleyite. They reported the structure as orthorhombic, although these authors observed deviations from orthorhombic symmetry as splitting of some diffraction maxima in synchrotron radiation (personal communication). Kohlstedt et al. (1996) measured the solubility of H in Fo $_{90}$ olivine, wadsleyite, and ringwoodite [γ -(Mg,Fe) $_2$ SiO $_4$]. They reported up to 2.4 wt% H $_2$ O in wadsleyite, 2.7 wt% in ringwoodite, but only 0.12 wt% in olivine.

Kawamoto et al. (1996) have investigated the phase relations of a hydrous natural peridotite and estimated partition coefficients of H between hydrous ultramafic melts, wadsleyite, and ringwoodite. They postulated a hydrous transition zone through cooling of a hydrous magma ocean. To assess the mechanism of H incorporation and the effect of Fe on the crystal structure of hydrous wadsleyite, we have conducted further experiments in peridotite systems to produce crystals of sufficient grain size for single-crystal X-ray diffraction. Smyth and Kawamoto (1997) observed a new structure with composition Fo_{91} and Fo_{88} and determined the crystal structure of the Fo_{91} sample. Termed wadsleyite II, it is a hydrous spinelloid similar to wadsleyite, but with a b axis 2.5 times greater. This structure appeared in experiments with $\text{Mg}/(\text{Fe} + \text{Mg})$ ratios of 0.82 and at pressures greater than 17 GPa. The sample contains a partially occupied Si tetrahedron adjacent to a partially occupied Mg-Fe octahedron that, together, were postulated to be the result of decompression of a single Mg-Si octahedron. Experiments with lower Fe contents produced $\text{Fo}_{94.6}$ hydrous wadsleyite, which proved to be monoclinic. We report here the structure of one of these monoclinic crystals.

EXPERIMENTAL METHODS

The starting material for the experiment was a mixture of Mg-free KLB-1 peridotite gel and brucite, resulting in an overall H_2O content of 13.6 wt% and an $\text{Mg}/(\text{Mg} + \text{Fe})$ atomic ratio of 0.90. Double-wrapped Re foil was used as a heater outside an $\text{Au}_{75}\text{Pd}_{25}$ capsule in a multi-anvil high-pressure device (Walker et al. 1990). The experiment conditions were 17 ± 1 GPa and 1400 °C with a duration of 17 h. The experimental products were composed of a light olive-green majorite garnet, a dark green wadsleyite, and dendritic-textured quenched partial melt. Grain sizes of the wadsleyite are up to 200 μm .

The major-element compositions of phases were determined by electron microprobe. H concentrations were determined with a secondary ion mass spectrometer (SIMS) at the Center for Solid State Science, Arizona State University, following the procedures outlined in Ihinger et al. (1994). The ion beam diameter was ~ 20 μm . Chemical compositions of the wadsleyite fall roughly between olivine and phase E. Hence, we used the olivine-phase E calibration to quantify the H^+ signal in the sample by assuming that olivine is anhydrous and the H_2O content of phase E is 7.6 wt% (Inoue et al. 1995). The chemical composition of the sample is given in Table 1.

A crystal approximately $50 \times 60 \times 100$ μm was separated from a polished mount of the sample. The orientation was determined by means of a rotation photograph, and the unit cell refined from centering of 16 nonequivalent X-ray reflections each at both positive and negative 2θ positions. Nonlinear least-squares refinement of the unit-cell parameters gave $a = 5.6715(7)$, $b = 11.5820(16)$, $c = 8.2576(11)$ Å, and $\beta = 90.397(9)^\circ$ with a monoclinic, body-centered lattice. All reflections were sharp with typical peak widths of $0.6^\circ 2\theta$. There was no

TABLE 1. Chemical analysis and unit-cell parameters of monoclinic hydrous wadsleyite from electron microprobe, SIMS, and X-ray single-crystal diffraction

Oxide weight percent	
SiO_2	41.72(42)
Al_2O_3	0.29(2)
FeO	4.95(18)
MgO	48.85(31)
CaO	0.00(0)
H_2O	2.24(18)
Total	98.05
Cations per 4 O atoms	
Si	0.991
Al	0.008
Fe	0.098
Mg	1.730
Ca	0.000
H	0.355
a (Å)	5.6715(7)
b (Å)	11.582(2)
c (Å)	8.258(1)
β ($^\circ$)	90.397(9)
V (Å ³)	542.43(12)
Density (g/cm ³)	3.511

evidence of peak splitting as might be expected from twinning on a mirror perpendicular to a , the operation violated in the drop to monoclinic symmetry. An octant of intensity data with $3.5 < 2\theta < 30^\circ$ was measured without the lattice constraint, and no violations of the body centering were observed. A hemisphere of intensity data was then measured to $2\theta = 65^\circ$ with the I lattice constraint using ω scans with scan rates variable from 2 to 10° ω per minute. With the X-ray generator operating at 50 KV and 280 Ma, data collection yielded 1784 measured intensities of which 830 were unique, and, of these, 650 were greater than 4σ above background. The mean I/σ was 21.2 for all reflections. The data were corrected for Lorentz and polarization effects and for absorption using an analytical absorption correction routine based on the measured shape of the crystal. The space groups determined from the observed intensities were $I2/m$, plus the possible acentric subgroups $I2$ and Im . The nonstandard setting of $C2/m$ was chosen to preserve the wadsleyite cell and atom coordinates.

The data for equivalent reflections were averaged with an R_{int} of 0.007. The initial atom positions were taken from Finger et al. (1993), plus those sites that become nonequivalent with lowering of symmetry. In the lower symmetry, M3 has two nonequivalent positions, M3a and M3b, as does O4: O4a and O4b. Otherwise, site nomenclature is that of wadsleyite. The structure was refined in space group $I2/m$ using the program SHELXTL (Sheldrick 1990). Scattering factors for neutral atoms were used throughout. The M-site occupancies were modeled with a scattering curve for neutral Fe only and occupancies reported in numbers of electrons (refined Fe occupancy times 26 divided by equipoint fraction). The occupancies of the two nonequivalent M3 sites appear to differ by about 10σ .

TABLE 2. Final position, occupancy, and displacement parameters for hydrous wadsleyite in space group $I2/m$

Atom	x/a	y/b	z/c	Occ.*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
M1	0	0	0	11.08(9)	0.0242(9)	0.0117(6)	0.0247(3)	0.0006(4)	0.0033(6)	0.0035(3)	0.0202(5)
M2	0.0012(2)	¼	0.9709(1)	11.08(6)	0.0163(7)	0.0104(5)	0.0123(5)	0	0.0001(3)	0	0.0132(3)
M3a	¼	0.1222(1)	¼	9.20(5)	0.0139(6)	0.0175(6)	0.0137(6)	0	-0.0015(4)	0	0.0150(3)
M3b	¼	0.3783(1)	¼	9.98(5)	0.0149(6)	0.0167(6)	0.0130(5)	0	0.0019(4)	0	0.0149(3)
Si	0.0002(1)	0.12123(5)	0.61558(6)	0.913(4)	0.0096(3)	0.0066(2)	0.0088(2)	0.0003(3)	0.0000(2)	-0.0004(2)	0.0083(1)
Si2	0.498(4)	0.137(2)	0.128(2)	0.024(2)							0.014(2)
O1	-0.0006(5)	¼	0.2256(3)	0.5	0.012(1)	0.016(1)	0.017(1)	0	0.0000(8)	0	0.0149(6)
O2	-0.0008(5)	¼	0.7166(2)	0.5	0.015(1)	0.0117(9)	0.0133(9)	0	0.0004(8)	0	0.0135(6)
O3	0.0007(4)	0.0124(1)	0.7436(2)	1.00	0.016(1)	0.0157(7)	0.0160(7)	0.0002(6)	-0.0008(6)	-0.0001(5)	0.0159(5)
O4a	0.2601(2)	0.1242(1)	0.9946(2)	1.00	0.0134(7)	0.0100(6)	0.0166(6)	0.0004(7)	-0.0006(5)	0.0008(6)	0.0134(4)
O4b	0.7412(2)	0.3759(1)	0.9956(2)	1.00	0.0131(7)	0.0096(6)	0.0159(6)	0.0005(7)	0.0001(5)	0.0000(6)	0.0128(4)
H1	0.016(2)	¼	0.285(7)	0.27(4)							0.05

* Occupancy for M sites given as number of electrons (see text).

A difference Fourier was calculated to look for possible H positions. The largest residual occurred at $x/a = 0.50$, $y/b = 0.14$, and $z/c = 0.13$, in a normally vacant tetrahedral void adjacent to M3a and M3b, 1.7 Å from the nearest O atom. This position is not a likely location for an H atom, but is analogous to the Si3 position in wadsleyite II (Smyth and Kawamoto 1997). An Si atom, Si2, was placed in this site in the model, and its occupancy refined to 2.4%, which reduced the R value from 3.4 to 3.0%. The occupancy of the Si1 position was then

refined and its value declined to 92%, which further reduced the R value to 2.7%.

Several small residuals remained, but all were less than 0.4 e^- . The largest of these is at $x/a = 0.015$, $y/b = 0.25$, and $z/c = 0.32$. This is approximately the position predicted by Smyth (1994). An H atom was placed at this position in the model and positional parameters refined. The positional and occupancy parameters refined to stable values with U_{iso} fixed at 0.05, and the R value reduced slightly to 2.6%. There remained an additional residual near O3 at $x/a = 0.75$, $y/b = 0.11$, and $z/c = 0.75$ that might be a second H position. However, its distance from O3 was 1.1 Å, which is longer than O-H distances commonly found in X-ray structure refinements. Other residuals were less than 0.25 e^- . The final refinement converged to an R value of 2.6% (R_w of 0.024). The final positional, occupancy, and displacement parameters are reported in Table 2. Nearest-neighbor cation-O atom distances are given in Table 3 along with polyhedral volume and distortion parameters. A polyhedral drawing of the structure showing Si and H positions in approximately [001] projection is given as Figure 1.

TABLE 3. Selected cation-O atom distances (Å) and coordination polyhedron parameters in monoclinic hydrous wadsleyite

M1		M2	
Pt. Sym.	i	Pt. Sym.	m
O3 × 2	2.123(2)	O1	2.104(3)
O4a × 2	2.061(2)	O2	2.100(2)
O4b × 2	2.054(2)	O4a × 2	2.077(2)
		O4b × 2	2.084(2)
Mean	2.076	Mean	2.088
Poly. Vol*	11.92	Poly. Vol*	12.02
O.Q.E.**	1.0037	O.Q.E.**	1.0063
A.V.†	11.52	A.V.†	22.38
M3a		M3b	
Pt. Sym.	i	Pt. Sym.	m
O1 × 2	2.061(2)	O1 × 2	2.062(2)
O3 × 2	2.111(2)	O3 × 2	2.101(2)
O4a × 2	2.111(1)	O4b × 2	2.102(1)
Mean	2.094	Mean	2.088
Poly. Vol*	12.17	Poly. Vol*	12.06
O.Q.E.**	1.0044	O.Q.E.**	1.0048
A.V.†	15.12	A.V.†	16.96
Si1		Si2	
Pt. Sym.	i	Pt. Sym.	m
O2	1.709(1)	O1	1.78(2)
O3	1.645(2)	O3	1.98(2)
O4a	1.641(2)	O4a	1.74(2)
O4b	1.643(1)	O4b	1.77(2)
Mean	1.660	Mean	1.82
Poly. Vol*	2.336	Poly. Vol*	3.02
T.Q.E.‡	1.0034	T.Q.E.‡	1.017
A.V.†	13.69	A.V.†	65.

* Polyhedral volume in Å³.

** Octahedral quadratic elongation (Robinson et al. 1971).

† Variance of central angle.

‡ Tetrahedral quadratic elongation (Robinson et al. 1971).

DISCUSSION

Kudoh et al. (1996) reported the crystal structure of an Fe-free hydrous wadsleyite with 3.3 wt% H₂O crystallized at 1300 °C and 15.5 GPa. The small size of the crystal (4.2 × 10⁻⁸ cm³) limited the number of observed X-ray data and, to a lesser extent, the precision to which cell parameters could be determined. They reported the space group of the sample as *Imma* (orthorhombic) and refined the structure with that symmetry. These authors have, however, reported monoclinic symmetry in several of their specimens (Y. Kudoh, T. Inoue, personal communication). Their structure analysis, together with IR and Raman spectra, strongly favors protonation of O1 as suggested by Smyth (1987), rather than O2 as favored by Downs (1989). However, their observed 17% site vacancy in M3 and suggested H location were not predicted by Smyth (1994).

The results of the current study are in generally good

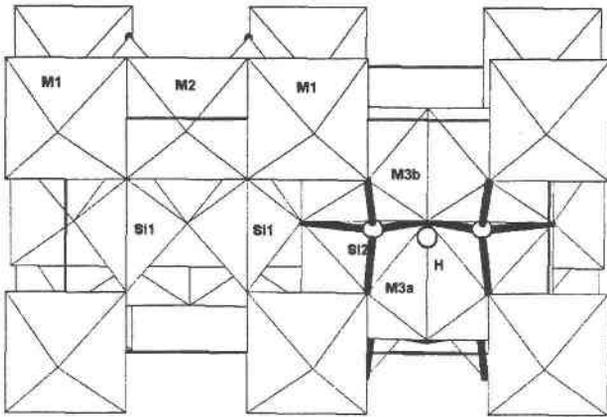


FIGURE 1. Crystal structure of monoclinic hydrous wadsleyite (b is horizontal), projected approximately down [001]. The H position (labeled) is directly above O1, the oxygen shared by the four M3 cations. In the monoclinic structure, there are two nonequivalent M3 sites labeled M3a and M3b. An extra Si position with about 3% occupancy, shown with heavy lines as bonds to adjacent O positions, was observed adjacent to the M3 octahedra and is postulated to be the result of partial Si occupancy of M3a at high pressure.

agreement with those of Kudoh et al. (1996) with some refinements. Both studies report the most vacancy in M3 with smaller vacancies in M1 and M2. Anisotropic atomic displacement parameters are also in good agreement. Both studies report an expansion of b and contraction of a with hydration. Both studies show significantly increased O1-M distances relative to anhydrous wadsleyite, which is consistent with hydration of O1. Furthermore, the mean cation-O distance around O1 appears to increase with increasing hydration. In this structure, O1 is bonded to five M sites: two M3a, two M3b, and one M2 site. In anhydrous Fo_{92} and Fo_{100} wadsleyite, the mean O1-M distances are 2.029(2) and 2.030(2) Å, respectively (Finger et al. 1993). In the current structure with 2.24 wt% H_2O , the mean O1-M distance is 2.070(2) Å, whereas it is 2.080(6) Å in the Fo_{100} structure reported by Kudoh et al. (1996).

The total volume of the current crystal is approximately ten times that studied by Kudoh et al. (1996). The current sample also contains Fe with $\text{Mg}/(\text{Fe} + \text{Mg}) = 0.946$, has less H, and was synthesized at slightly higher temperature (1400 °C) and pressure (17 ± 1 GPa). The increased crystal volume, together with the slightly more intense X-ray source, yielded a small improvement in cell parameter precision and a significant increase in number of observed intensities, which improved precision in the atom parameters.

New observations in the current study are that the structure can be monoclinic rather than orthorhombic, and that Si vacancy is significant. The β angle is $90.397(9)^\circ$, which differs from 90° by 40σ . Violation of orthorhombic symmetry is apparently caused by the ordering of vacancies and divalent cations into two nonequivalent M3 sites.

The refined occupancy of M3a is apparently less than that of M3b by approximately 15σ (Table 2). M3a is also slightly larger (Table 3). The presence of the extra Si site is curious and has not been noted previously. Smyth and Kawamoto (1997) observed an analogous site in wadsleyite II, with occupancy factor of 48%, and postulated that it was the result of decompression of an Mg-Si octahedron, with the Si moving to an adjacent tetrahedral void on release of pressure. If this hypothesis is correct, it may be that some of the observed M3 vacancy was Si occupancy and that deviation from orthorhombic symmetry is the result of Si ordering into one of two M3 sites. These hypotheses can, of course, only be rigorously tested by structure studies at high pressure.

If the deviation from orthorhombic symmetry is, indeed, caused by partial Si occupancy of M3, it might be expected to increase with pressure as Si moves toward octahedral coordination with pressure. This may help to explain why only some samples of hydrous wadsleyite show monoclinic symmetry. The crystal of Fe-free hydrous wadsleyite studied by Kudoh et al. (1996), grown at slightly lower pressure (15.5 GPa), has a higher H content than the current sample but apparently has orthorhombic symmetry. These authors have, however, reported other samples with monoclinic symmetry and β angles up to 90.2° (Y. Kudoh, personal communication). However, deviations from orthorhombic symmetry are small, so they are unlikely to alter the conclusion of Kudoh et al. (1996) that there is probably complete crystalline solution between hydrous and anhydrous wadsleyite, at least between compositions $\text{Fo}_{94.6}$ and Fo_{100} .

Experiments conducted at higher Fe contents [$\text{Mg}/(\text{Mg} + \text{Fe}) = 0.822$] at 17.5 ± 1 GPa and 18.0 ± 1 GPa produced wadsleyite II with $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios of 0.906 and 0.881, respectively (Smyth and Kawamoto 1997). The pressures of these more Fe-rich experiments were nominally slightly higher, but all pressures are the same within error. Wadsleyite II has not been reported in anhydrous experiments or in experiments at low Fe contents; however, wadsleyite and wadsleyite II cannot be easily distinguished by X-ray powder diffraction and are similar optically. Structure studies indicating possible octahedral Si in monoclinic hydrous wadsleyite as well as wadsleyite II, suggest that pressure may be a very important variable controlling the relative stabilities of these phases. However, experimental evidence currently favors Fe content as the controlling variable. More experiments are required to evaluate the effects of these variables.

Smyth (1994) postulated a model for hydration of wadsleyite that couples M2 site vacancy with hydration of O1 with symmetry reduced from body-centered to primitive orthorhombic. The hydration of O1 appears to be correct, rather than hydration of O2 as proposed by Downs (1989). However, as reported by Kudoh et al. (1996), the cation vacancy appears to be in M3 rather than M2. The determination of the H position from X-ray data is, at best, problematic. All that is visible is a very small perturbation in the electron density that

may or may not correspond to the proton position. However, the difference maximum was the largest within 1.0 Å of any O atom, and the H position parameters refined to stable values with precisions of approximately 0.1 Å. The position does result in a short O-H distance (0.7 Å) relative to positions determined by neutron diffraction, but this is typical for H positions determined from X-ray data. The H position is near O1 and lies on the mirror plane in approximately the position considered by Smyth (1994).

Finally, it is interesting to compare the current results on Fe ordering with those obtained by Finger et al. (1993) who observed a significant preference of Fe for M1 and M3 relative to M2 in Fe-bearing anhydrous wadsleyite. In contrast, we observed equal scattering by M1 and M2, but less scattering by either of the M3 sites. In the monoclinic structure, there are two nonequivalent M3 sites that differ in their apparent scattering by some 15σ . Because of the presence of vacancies in the monoclinic structure, we cannot unambiguously assign the observed scattering between Fe, Mg, and vacancy. Also, we do not know the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in this sample. However, it appears that both M3 sites have fewer electrons than expected for full occupancy by Mg. So, we can say with some confidence that there is significant site vacancy at both M3 sites and that M3a has more vacancies than M3b. The M3a site is also consistently larger, with corresponding O distances up to 10σ larger than in M3b. Thus, it appears that M-site cation vacancies are concentrated in M3 and no apparent ordering of Fe exists between M1 and M2.

In summary, this study has shown that cation vacancies in Si sites as well as in M3 are major charge compensation mechanisms that allow wadsleyite to incorporate variable amounts of H. The space group of the Fo_{95} specimen with 2.24 wt% H_2O is $I2/m$ (monoclinic) rather than $Imma$ (orthorhombic). Deviation from orthorhombic symmetry appears to result from ordering of vacancies, divalent cations, and possibly Si into two nonequivalent M3 sites. If this is caused by partial Si occupancy of M3, the deviation might be expected to increase with pressure. The monoclinic symmetry may be limited to crystals with low Fe content ($\text{Fo} > 92$) because a different but related structure, hydrous wadsleyite II, was observed in experiments with higher Fe contents (Smyth and Kawamoto 1997). Because $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios of the transition zone of the Earth's mantle are believed to be about 0.9, it is more likely that hydrous wadsleyite has the wadsleyite II structure, rather than the monoclinic structure in nature. However, further experiments, together with careful phase identification, will be required to constrain the relative stabilities of the complex hydrous spinelloids that appear to be possible constituents of the transition zone of the mantle.

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