LETTER

A crystallographic model for hydrous wadsleyite (β-Mg$_2$SiO$_4$): An ocean in the Earth's interior?

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Abstract

Using simple ionic constraints and maximal subgroup symmetry, a hypothetical, ordered model for hydrous wadsleyite has been created and examined. The model has formula $Mg_7Si_4O_{14}(OH)_2$, space group *Pmmb*, and an ordered vacancy into one of two nonequivalent M2 sites. It contains two H positions on the nonequivalent O1 sites. The model predicts strong c-axis polarization of IR and Raman O-H stretching absorptions. Electrostatic calculations indicate that hydration would relieve the underbonding of O1 as well as the overbonding of the bridging O2. The model predicts that the partial hydration of O2 suggested by Downs (1989) would result in a greater distortion of the silicate tetrahedra, whereas full hydration of O1 would decrease distortion of the tetrahedron. The model predicts that, under hydrous conditions, trivalent octahedral cations Fe^{3+}, Cr^{3+}, and Al^{3+} should be more soluble in wadsleyite than in olivine. Finally, the model predicts a maximum H_2O content for the hypothetical phase of 3.3 wt%. This implies that the transition zone of the mantle might contain several oceans of H_2O if fully hydrated.

Introduction

There has been considerable discussion in the recent literature about hydrous magnesium silicates in the upper mantle and transition zone. The stability of various stoichiometrically hydrous phases has been reviewed by Thompson (1992). Also, Bell and Rossman (1992) reviewed the H contents of nominally anhydrous phases that can contain trace to minor amounts of H and pointed out that these phases may contain an amount of H equal to a considerable fraction of the total amount of H in the hydrosphere of the Earth. With the exception of phase F (Kudoh et al., 1994), most of the stoichiometrically hydrous magnesium silicates contain more than two Mg atoms per Si and therefore would be unlikely to coexist with orthopyroxene or other silicates with a cation to O ratio <0.75 or a Mg-Si ratio of 1.0.

Of the nominally anhydrous phases believed to make up the upper mantle and transition zone, none has been reported with a greater H content than wadsleyite (β-Mg$_2$SiO$_4$). On the basis of IR spectroscopy, McMillan et al. (1991) reported that a pure Mg end-member wadsleyite contained about 5000 ppm OH (H per 10^6 Si). Young et al. (1993) reported a very much more hydrous Fe-bearing wadsleyite, with up to 60000 H per 10^6 Si. That would require about 1.5% of the O atoms to be OH molecules.

Wadsleyite has a very unusual crystal structure in that, unlike the orthosilicate α (olivine) and γ (spinel) polymorphs of Mg$_2$SiO$_4$, it is a soro-silicate. It contains Si$_2$O$_7$ groups rather than isolated SiO$_4$ tetrahedra. Smyth (1987), using a simple ionic model, predicted that this unusual crystal structure might be capable of containing considerable amounts of H as OH on the severely underbonded O1 atom, which is bonded to 5Mg and not to Si. According to a point-charge Madelung calculation, this O site has an anomalously shallow electrostatic potential (21.3 V), whereas the bridging O site has an anomalously deep potential (30.9 V) and the longest Si-O bond of any magnesium silicate. Downs (1989) used the X-ray data of Horiuchi and Sawamoto (1981) to estimate electron densities throughout this structure and located a possible protonation site on the overbonded O2 atom. This conclusion is at odds with the simple ionic model that led to the initial prediction of wadsleyite as a possible H host in the upper mantle. The ionic model, together with some crystallographic symmetry considerations, leads, however, to some very specific predictions about H location, IR spectral polarization, charge compensation mechanisms, polyhedral distortions, and cation substitutions, all of which may be used to test the model. The objectives of this letter are to explore some of these considerations, to present a model for the incorporation of H in wadsleyite, and to discuss the means by which the model may be tested and refined.
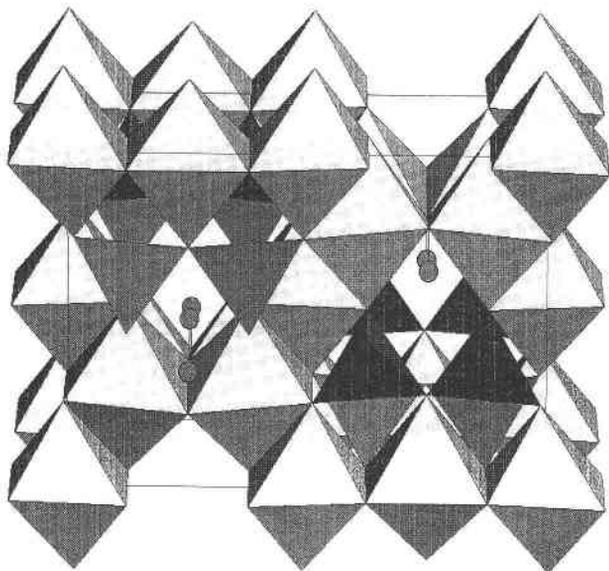
Fig. 1. Polyhedral representation of the crystal structure of hydrous wadsleyite (**c** is vertical, **b** is horizontal). The hydrated O2 atom lies at the center of four edge-sharing Mg3 octahedra.

TABLE 1. Nearest neighbor distances and site potentials for pure Mg end-member wadsleyite

Atom	Wyck. not.	Point symm.	Potential (V)	Neighbor	Dist. (Å)
Mg1	4a	2/m	−25.37	O3 × 2	2.113
				O4 × 4	2.047
Mg2	4e	mm	−25.34	O1 × 1	2.051
				O2 × 2	2.091
				O4 × 4	2.088
Mg3	8g	2	−25.93	O1 × 2	2.025
				O3 × 2	2.118
				O4 × 2	2.123
Si	8h	m	−46.76	O2 × 1	1.703
				O3 × 1	1.640
				O4 × 2	1.634
O1	4e	mm	21.28	Mg2 × 1	2.051
				Mg3 × 4	2.025
O2	4e	mm	30.94	Si × 2	1.703
				Mg2 × 1	2.091
O3	8h	m	26.78	Si × 1	1.640
				Mg1 × 1	2.113
				Mg3 × 2	2.118
O4	16j	1	26.97	Si × 1	1.634
				Mg1 × 1	2.047
				Mg2 × 1	2.088
				Mg3 × 1	2.123

THE WADSLEYITE STRUCTURE

The crystal structure of wadsleyite is illustrated in Figure 1. The space group is *Imma* (orthorhombic). The various atoms that compose the asymmetric unit and their nearest neighbor distances as determined by Finger et al. (1993) for pure Mg end-member wadsleyite are given in Table 1. There are three Mg sites, Mg1, Mg2, and Mg3, a single Si, and four O sites, O1, O2, O3, and O4. Mg1 is in the 4a position at the origin (0,0,0) with point symmetry 2/m. Mg2 is in a 4e position at (0,¼,z) with point symmetry *mm*. Mg3 is in an 8g position at (¼,y,¼) with point symmetry 2. The Si site is in an 8h position at (0,y,z) with point symmetry *m*. O1 and O2 are both in 4e positions, O3 is in an 8h position, and O4 is in the 16j general position. Each Mg is in a fairly regular octahedron. The Si is in a distorted tetrahedron with a very long Si-O bond (>1.70 Å) to O2, the bridging O atom. O1 is bonded to four M3 atoms and one M2 atom and is the only O not bonded to Si. O2 is the bridging O atom, bonded to two Si and one Mg (Mg2). O3 and O4 are similar to the O sites in olivine and γ-spinel and are each bonded to three Mg and one Si.

The site potentials computed from a simple point-charge model are given in Table 1. The O1 is severely underbonded and is the obvious candidate for hydration. The work of Young et al. (1993) showed considerable H in the structure, enough for 12% of the O1 positions to be OH. (There are half as many O1 atoms as Si.) If all the H were ordered into one site, there might be enough OH and Mg vacancies to alter the symmetry of the structure. The question arises then, is there a subgroup of *Imma* that would permit a fully ordered hydrous structure with ordered vacancies? If so, it would allow us to predict the H positions and possibly to calculate an energy of the structure. To facilitate energy calculations, both electrostatic and full-structure electron energy calculations such as those done for stishovite (Sherman, 1993), we chose the highest symmetry consistent with full order (sites fully occupied with one type of atom). Although not a unique solution, since many low-symmetry structures may allow such a configuration, there appears to be at least one subgroup that preserves orthorhombic symmetry.

The addition of significant amounts of H to the structure requires a charge compensation mechanism. A small trivalent atom could substitute for Si, but B is the only trivalent atom small enough and is too rare to be effective. A small monovalent atom could substitute for Mg, but Li is also too low in abundance to be significant in the mantle. Smyth (1987) suggested a Mg site vacancy, and that seems the most likely mechanism. To minimize charge separation, we assign the vacancy to an M site that is bonded to O1. From Table 1 we see that this criterion excludes M1. We would also prefer a high-symmetry, low-multiplicity position so that we can create an ordered structure with the least amount of H and vacancy, and so we prefer Mg2 over Mg3. Also, from Table 2 we see that M2 has the shallowest electrostatic potential (although not by much), and so the electrostatic energy is minimized if we choose Mg2 for partial vacancy. Also we see that Mg2 and O1 have the same point symmetry (*mm*) and multiplicity.

If we fully hydrate the O1 positions, we need to vacate one-half of the Mg2 sites. We would therefore like to identify a subgroup of *Imma* that splits Mg2 into two nonequivalent sites. This entails retaining the *mm* point symmetry of the site. The centric orthorhombic subgroups of *Imma* are *Pmmb, Pmma, Pnna, Pnnb, Pnma, Pnmb, Pmna,* and *Pmnb*. Of these subgroups, only *Pmmb*

TABLE 2. Nearest neighbor distances and site potentials for hypothetical hydrous wadsleyite

Atom	Wyck. not.	Point symm.	Potential (V)	Neighbor	Dist. (Å)
Mg1a	2a	2/m	−24.62	O3a × 2	2.113
				O4a × 4	2.047
Mg1b	2d	2/m	−27.22	O3b × 2	2.113
				O4b × 4	2.047
Mg2	2e	mm	−24.52	O1a × 1	2.052
				O2a × 1	2.090
				O4a × 4	2.088
Mg3	8f	1	−23.19	O1a × 1	2.025
				O1b × 1	2.025
				O3a × 2	2.118
				O3b × 2	2.118
				O4a × 2	2.123
				O4b × 2	2.123
Sia	4i	m	−47.40	O2a × 1	1.703
				O3a × 1	1.640
				O4b × 2	1.634
Sib	4i	m	−47.60	O2b × 1	1.703
				O3b × 1	1.640
				O4a × 2	1.634
Ha	2e	mm	−15.59	O1a	1.050
Hb	2f	mm	−23.80	O1b	1.050
O1a	2e	mm	30.71	Ha	1.050
				Mg2 × 1	2.051
				Mg3 × 4	2.025
O1b	2f	mm	27.20	Hb	1.050
				Mg3 × 4	2.025
O2a	2e	mm	29.38	Sia × 2	1.703
				Mg2 × 1	2.091
O2b	2f	mm	26.62	Sib × 2	1.703
O3a	4i	m	27.26	Sia × 1	1.640
				Mg1a × 1	2.113
				Mg3a × 2	2.118
O3b	4j	m	26.19	Sib × 1	1.640
				Mg1b × 1	2.113
				Mg3 × 2	2.118
O4a	8l	1	27.57	Sib × 1	1.634
				Mg1a × 1	2.047
				Mg2 × 1	2.088
				Mg3 × 1	2.123
O4	8l	1	25.49	Sia × 1	1.634
				Mg1b × 1	2.047
				Mg3 × 1	2.123

TABLE 3. Atom positions for hypothetical hydrous wadsleyite in space group *Pmmb*

Atom	x	y	z
Mg1a	0	0	0
Mg1b	½	½	½
Mg2	0	¼	0.9701
Mg3	0.250	0.1264	0.250
Ha	0	¼	0.3459
Hb	½	¾	0.5915
Sia	0	0.1201	0.6166
Sib	½	0.6201	0.1166
O1a	0	¼	0.2187
O1b	½	¾	0.7187
O2a	0	¼	0.7168
O2b	½	¾	0.2168
O3a	0	0.9895	0.2556
O3b	½	0.4895	0.7556
O4a	0.2698	0.1229	0.9929
O4b	0.7608	0.6229	0.4929

dictions that can readily be tested with experimental studies. First, the model has two distinct H sites, both with point symmetry *mm* and both with O-H vectors parallel to c. The model thus predicts a strong c-axis polarization of the IR and Raman OH stretching absorptions and two distinct absorption frequencies. McMillan et al. (1991) and Young et al. (1993) both reported strong absorption features at about 3329 cm^{-1} and a weaker multiple feature near 3600 cm^{-1}. Neither of these groups reported polarized spectra from oriented specimens, and so polarization is as yet unknown. The prediction of very strong polarization does serve as a warning about quantitative interpretation of IR spectra from randomly oriented single crystals to estimate OH contents.

The second significant feature of the model is the site potentials. Full protonation of the O1 positions greatly relieves the underbonding of these O sites, deepening the site potentials to levels commonly observed for O sites in silicates and oxides (Smyth, 1988) and reducing the range of potentials in this structure by about a factor of two. Further, protonation of O1, coupled with vacating half of the M2 sites, relieves the overbonding of O2. That would have the effect of reducing the gross distortion of the silicate tetrahedra observed in this structure. The site potentials of the fully protonated model are thus more in line with those observed in common silicates than with those of the anhydrous structure. This implies that the hydrated model structure may be more stable than the anhydrous structure, which might expand its stability field in the mantle.

Downs (1989) examined the electrostatic potentials in wadsleyite derived from a covalent model of electron distribution rather than from a simple point-charge model. He concluded that there were two possible protonation sites, one on O1, as Smyth (1987) predicted, and another on the O2 bridging O site. Young et al. (1993) interpreted the IR spectra as indicating that both positions were occupied. Downs's prediction of the second protonation site on O2 is somewhat at odds with the simple point-charge model and with observation of OH positions on other silicates. There is not a single example of OH occupying

retains the *mm* point symmetry of the 4e positions and splits the four into two nonequivalent sites (Wyckoff notation 2e and 2f in space group *Pmmb*), each with a multiplicity of two. This allow us to put one H in a 2e site on O1a and another H in a 2f site on O1b. If the H atoms retain the same *mm* point symmetry and multiplicity as their host O, the OH vector is constrained to lie parallel to c. If we arbitrarily set the O-H distance at 1.05 Å, we obtain positions for both the H atoms. These positions are given in Table 3, and the point symmetries and nearest neighbor distances are given in Table 2. The H positions selected would not be equivalent in *Imma*. Hb lies within a vacated M2 octahedron, whereas Ha lies opposite the occupied Mg2 site.

DISCUSSION

Using a simple ionic approach, and selecting a subgroup to maximize symmetry consistent with full order, we have created a hypothetical ordered structure for a fully hydrated form of β-Mg$_2$SiO$_4$. The model has several features of possible significance. These features allow pre-

a bridging O position between two tetrahedral Si atoms among natural silicates. The simple ionic interpretation of this is that protonation of these O atoms would deepen the site potential to unreasonable values, which would further lengthen the Si-O(br) bond and further distort the tetrahedra. The Si-O(br) bond in wadsleyite, at 1.70 Å, is already longer than that in any other common silicate.

However, a proton on a bridging O would be an interesting phenomenon to evaluate using the point-charge model. A proton was placed in the model in a $2e$ position in the vacant M2 site, near the position predicted by Downs (1989). The potential obtained for this site was -19.5 V, which is slightly more favorable than that calculated for the Ha site of our model hydrous structure (Table 2). However, the effect on the other site potentials more than offsets this difference. The hydrated bridging O potential increased to 35.7 V, well outside the range observed for other silicate O sites by $>10\%$. The unhydrated O1 potential returned to the very low values of the anhydrous structure. Although partial protonation of this site cannot be ruled out, the ionic model indicates that the two IR absorption features are due to the two proton positions on O1, one being adjacent to a vacant M2 and the other adjacent to an occupied M2. The question of where the second H is located could be resolved with a crystal structure refinement of a hydrous wadsleyite sample. A more distorted Si tetrahedron in the hydrous structure would indicate partial hydration of O2, whereas a less distorted Si site would indicate protonation of O1 only.

The third significant feature of the model is its Mg-Si ratio. With a formula of $Mg_7Si_4O_{14}(OH)_2$, the model structure has a Mg-Si ratio of 1.75, which is intermediate between olivine (2) and orthopyroxene (1), as is that of the pyrolite model of mantle composition at about 1.3 (Ringwood, 1979). This means that both olivine and orthopyroxene would be consumed by this phase below 400 km if H were present and that, unlike most high-pressure hydrous magnesium silicates such as phase B and superhydrous phase B (SHyB), hydrous wadsleyite would coexist with a phase of pyroxene stoichiometry such as majorite or ilmenite-structured $MgSiO_3$.

The fourth significant feature of the model is an indirect implication that trivalent cations, Fe^{3+}, Cr^{3+}, and Al^{3+} are more soluble in wadsleyite than in olivine. The apparent tolerance for protonation and vacancy give the structure some flexibility in the charge of the octahedral cation. Since there are two H positions, one might easily be vacant for charge compensation of an octahedral trivalent cation. An end-member with a formula $Mg_6(Fe^{3+}, Cr^{3+}, Al^{3+})Si_4O_{15}(OH)$ appears to be quite reasonable. This might explain the greater H contents of Fe-bearing wadsleyite than of pure Mg end-member wadsleyite (Young et al., 1993). It might also explain the anomalously high Fe content (Fa_{40}) of one of the wadsleyite samples described by Finger et al. (1993).

The fifth significant feature of the model structure is the limit established for the H content of this structure. The hypothetical hydrous end-member has the formula $Mg_7Si_4O_{14}(OH)_2$ and would thus contain 500 000 H atoms per 10^6 Si. In values of weight percent oxide, the pure magnesian variety would be 44.5% SiO_2, 52.2% MgO, and 3.33% H_2O. If the Earth's mantle between 400 and 525 km were 60% fully hydrated wadsleyite with a density of 3.5 g/cm³, the amount of H_2O incorporated in this phase would be equal to a worldwide ocean more than 8 km deep or more than four times the amount of H_2O currently in the Earth's hydrosphere. Because the amount of H_2O is so vast, one is reminded of Jules Verne's (1864) fictional explorer, Professor Lidenbrock, who discovered an ocean in the Earth's interior. However, evaluation of this interesting possibility in the current century will require laboratory exploration of the effect of H on the stability, structure, and physical properties of wadsleyite, rather than field work with ropes and ladders.

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