β-Mg$_2$SiO$_4$: A potential host for water in the mantle?

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Abstract

Electrostatic potentials and Pauling bond strengths have been calculated for a group of oxygen and hydroxyl sites in high-pressure silicate and oxide phases. The O1 position in β-Mg$_2$SiO$_4$ more closely resembles a hydroxyl than an oxygen in its electrostatic potential and coordination. This raises the possibility that β-Mg$_2$SiO$_4$ may be a host phase for water in the lower part of the upper mantle, if charge balance can be maintained by partial M-site vacancy as is typical of high-pressure pyroxenes. Partial hydroxyl occupancy of O1 is consistent with synthesis experiments, crystal-structure analysis, and Raman spectroscopic data, but further experimental work is required to confirm and evaluate the significance of this possibility. If it can be demonstrated experimentally that this does occur, there would be substantial consequences for geophysical and geochemical models of the upper mantle.

Introduction

Hydrous phases that are stable under temperature and pressure conditions of the upper mantle may exert a major control on melting relations and hence on petrologic and geochemical evolution of the mantle. Two hydrous phases that are common in high-pressure inclusions from kimberlites and alkali basalts are phlogopite and amphibole (pargasites, richterites, and kaersutites). Less common hydrous phases that may also be stable under mantle conditions include titanoclinohumite and titanochondrodite (Aoki et al., 1976; Yamamoto and Akimoto, 1977) plus apatite (e.g., Dawson, 1980). A 10-Å Mg phyllosilicate has been shown to be stable at pressures of 3.2 to 9.5 GPa (Akimoto and Akaogi, 1980; Bauer and Sclar, 1981). Hydrous garnet may also be a possible host for hydroxyl in the mantle; however, neither hydrous garnets nor the 10-Å Mg-phyllosilicate phase are known from inclusions in kimberlites or alkali basalts. Additionally, poorly characterized phases "A" and "B," both of which have higher Mg/Si ratios than forsterite, have been reported by several studies of the system MgO-SiO$_2$-H$_2$O (Akimoto and Akaogi, 1980; Liu, 1985).

Hydroxyl sites in minerals can usually be identified among the various oxygen sites in a crystal structure by electrostatic and Pauling bond-strength-summation methods without having to resort to neutron single-crystal diffraction to locate the H positions. Smyth and Bish (1987) have recently published an extensive series of electrostatic and cation-coordination-parameter calculations for most of the common rock-forming minerals including the more common phases believed to be present in the mantle. Using this mineral-structure database and a FORTRAN code from Y. Ohashi (ARCO Research, Plano, Texas, U.S.A.), electrostatic and coordination parameters for

oxygen sites in high-pressure silicate and oxide phases have been calculated to see if any of the anion sites in these phases might be able to accommodate hydroxyl.

Methods

Hydroxyl sites in silicates have several crystal-chemical characteristics in common by which they may commonly be distinguished from ordinary oxygen sites. First, they have low apparent Pauling bond-strength sums and thus are "undersaturated" relative to ordinary divalent oxygens. Second, they do not bond to Si: there are no mineral structures in which hydroxyl sites coordinate highly charged tetrahedral cations such as Si^{4+}, P^{5+}, or S^{6+}. Third, they tend to have low electrostatic potentials relative to oxygen.

Electrostatic potentials for over 1000 oxygen sites in minerals have been calculated from the database of Smyth and Bish (1987) using full nominal valence charges. In order to compare hydroxyl sites with nonhydroxyl oxygen sites, it is convenient to model the hydroxyl charge as a single charge of -1 at the oxygen center of the hydroxyl and normal oxygen as a charge of -2. The electrostatic energies thus obtained were divided by the charge to obtain a potential in volts. For a representative group of 280 (nonhydroxyl) oxygen sites in 62 common rock-forming silicates and oxides, the average potential was found to be 27.69 V (=electron volts per electron charge) with a standard deviation of 2.18 V. For a subset of these, 109 oxygen sites in 34 common orthosilicates and sorosilicates, the potential was 27.29 V with a standard deviation of 1.35 V.

Hydroxyl sites, by comparison, have much shallower potentials falling in the range of 5 to 22 V. Coordination and electrostatic parameters of several hydroxyl sites in

TABLE 1. Coordination and electrostatic parameters for some monovalent anion sites in high-pressure minerals

Structure	Site	Coordination	Pauling	Potential (V)	Structure reference
Cummingtonite	OH	3 Mg	1.00	12.3	Ghose (1961)
Pargasite	OH	3 (Mg, Fe)	1.00	11.3	Robinson et al. (1973a)
Phlogopite	F	3 Mg, 1 K	1.08	16.8	McCauley et al. (1973)
Norbergite	OH,F	3 Mg	1.00	11.6	Gibbs and Ribbe (1969)
Chondrodite	OH,F	3 Mg	1.00	10.9	Gibbs et al. (1970)
Humite	OH,F	3 Mg	1.00	10.6	Ribbe and Gibbs (1971)
Clinohumite	OH,F	3 Mg	1.00	10.3	Robinson et al. (1973b)
Topaz	OH,F	2 Al	1.00	13.3	Zemann et al. (1979)
Apatite	OH	3 Ca	0.75	13.2	Sudarsanan and Young (1969)
β-Mg$_2$SiO$_4$	O1	5 Mg	1.67	17.7	(see text)

minerals believed to be stable within the upper mantle are presented in Table 1. The average potential of these sites is 12.41 V with a standard deviation of 2.19 V.

In order to predict possible hydroxyl sites in high-pressure phases, electrostatic and coordination parameters were calculated for anion sites in high-pressure silicate and oxide phases for which crystal structures have been well determined. Parameters for oxygen sites in periclase (MgO), forsterite (α-Mg$_2$SiO$_4$), β-Mg$_2$SiO$_4$, γ-Mg$_2$SiO$_4$, pyrope, orthoenstatite, MgSiO$_3$ (ilmenite structure), MgSiO$_3$ (perovskite structure), jadeite, coesite, and stishovite are presented in Table 2. Of these 28 sites, four have low Pauling bond-strength sums: O(1) of β-Mg$_2$SiO$_4$,

O(2) of jadeite, and O(2a and 2b) of orthopyroxene. Of these four, only O(1) of β-Mg$_2$SiO$_4$ also has a low electrostatic potential, being nearly 5σ below the mean for orthosilicates and sorosilicates. Further, it is the only silicate oxygen in the group not bounded to Si. Thus, of the 28 oxygens examined, O(1) of β-Mg$_2$SiO$_4$ is the only site to meet all three criteria for potential hydroxyl sites described above. It appears then that β-Mg$_2$SiO$_4$ is a potential host for hydroxyl, and thus a possible source of water, within the lower part of the upper mantle.

The β-Mg$_2$SiO$_4$ structure is illustrated in Figure 1. It is not a spinel, as it is sometimes called, or even an orthosilicate. It is a sorosilicate with distinct Si$_2$O$_7$ groups. The

TABLE 2. Coordination and electrostatic parameters for oxygen sites in high-pressure silicates and oxides

Structure	Site	Coordination	Pauling	Potential (V)	Structure reference
Periclase	O	6 Mg	2.0	23.9	Hazen (1976)
Forsterite	O(1)	3 Mg, 1 Si	2.0	27.7	Fujino et al. (1981)
	O(2)	3 Mg, 1 Si	2.0	27.5	
	O(3)	3 Mg, 1 Si	2.0	26.3	
β-Mg$_2$SiO$_4$	O(1)	5 Mg	1.67	21.6	Horiuchi and Sawamoto (1981)
	O(2)	1 Mg, 2 Si	2.33	30.9	
	O(3)	3 Mg, 1 Si	2.00	26.7	
	O(4)	3 Mg, 1 Si	2.00	27.0	
γ-Mg$_2$SiO$_4$	O	3 Mg, 1 Si	2.00	26.6	Sasaki et al. (1982a)
Pyrope	O	2 Mg, 1 Al, 1 Si	2.00	27.1	Novak and Gibbs (1971)
Orthoenstatite	O(1a)	3 Mg, 1 Si	2.00	26.0	Sasaki et al. (1982b)
	O(1b)	3 Mg, 1 Si	2.00	26.4	
	O(2a)	2 Mg, 1 Si	1.67	26.4	
	O(2b)	2 Mg, 1 Si	1.67	26.5	
	O(3a)	1 Mg, 2 Si	2.33	30.9	
	O(3b)	1 Mg, 2 Si	2.33	30.6	
MgSiO$_3$ (ilmenite structure)	O	2 Mg, 2 Si	2.00	27.4	Horiuchi et al. (1982)
MgSiO$_3$ (perovskite structure)	O1	5 Mg, 2 Si	1.83	26.8	Yagi et al. (1978)
	O2	4 Mg, 2 Si	2.08	26.9	
Jadeite	O1	1 Na, 2 Al, 1 Si	2.13	27.5	Cameron et al. (1973)
	O2	1 Na, 1 Al, 1 Si	1.63	26.1	
	O3	2 Na, 2 Si	2.25	30.3	
Coesite	O1	2 Si	2.00	29.1	Smyth et al. (1987)
	O2	2 Si	2.00	29.6	
	O3	2 Si	2.00	30.7	
	O4	2 Si	2.00	30.4	
	O5	2 Si	2.00	31.0	
Stishovite	O	3 Si	2.00	28.6	Baur and Khan (1971)

crystal structure was determined from powder data by Moore and Smith (1970) and has since been refined from single-crystal X-ray data (Horiuchi and Sawamoto, 1981). In space group *Imma,* it has one distinct Si site (8h position with point symmetry m) and three distinct divalent metal sites: M1 (4a position, point symmetry 2/m), M2 (4e position, point symmetry mm), and M3 (8g position, point symmetry 2). It has four oxygens: O1 (4e position, point symmetry mm), O2 (4e position, point symmetry mm), O3 (8h position, point symmetry m), and O4 (16j general position). The O2 position is the bridging oxygen of the Si$_2$O$_7$ group and is also bonded to one M2, so it is oversaturated. It has the deepest electrostatic potential but is by no means atypical of bridging oxygens. By contrast, O1 is bonded to five Mg, but not to Si, and is thus undersaturated. More significantly, it has an anomalously shallow electrostatic potential that is lower than that of any other silicate or oxide oxygen studied and is nearly 5σ below the mean potential of other oxygens in orthosilicates and sorosilicates. Sites O3 and O4 are more normal oxygen positions in that they are exactly saturated (Pauling bond-strength sum = 2.00) and bond to three Mg and one Si as do all oxygens in the other Mg$_2$SiO$_4$ polymorphs.

In order for this structure to accommodate a hydroxyl or F in the O1 site, charge balance must be maintained. The usual way of doing this is to substitute a cation of lesser charge into one of the four cation sites. This would mean a monovalent cation in one of the M sites or a trivalent cation in the Si site. However, most monovalent cations are too large to substitute for Mg; the possible exception is Li, which does not appear to be sufficiently abundant in the mantle for this substitution to occur in significant quantity. Similarly, Al might substitute for Si, but Al is not found in tetrahedral coordination in minerals from pressures greater than about 2 GPa. B would be a viable substituent, but again, its abundance in the mantle is probably too low for it to be a significant substituent.

Another possible charge-balancing mechanism is partial M-site vacancy. Ca-Eskola pyroxene (Ca□Al₂Si₄O₁₂) appears to be a major vacancy-bearing constituent of mantle-derived omphacites (Wood and Henderson, 1978; Smyth, 1980; Gasparik and Lindsley, 1980; McCormick, 1986). Inasmuch as pyroxenes with at least 10% M2-site vacancy have equilibrated at pressures as high as 5 GPa (e.g., Khanukhova et al., 1977), partial M-site vacancy may be a viable mechanism for charge balance of substantial hydroxyl substitution in β-Mg₂SiO₄. In addition, the vacancy end-member pyroxene appears to be stabilized by temperatures in excess of 1250 °C (Smyth et al., 1984).

Indeed, there may be some evidence that this substitution does occur in β-Mg₂SiO₄. Many workers have found the β phase difficult to synthesize. Akaogi et al. (1984) synthesized β-Mg₂SiO₄ from a very fine-grained "reactive" forsterite that had been synthesized from hydrous starting materials. It is possible that residual hydroxyl
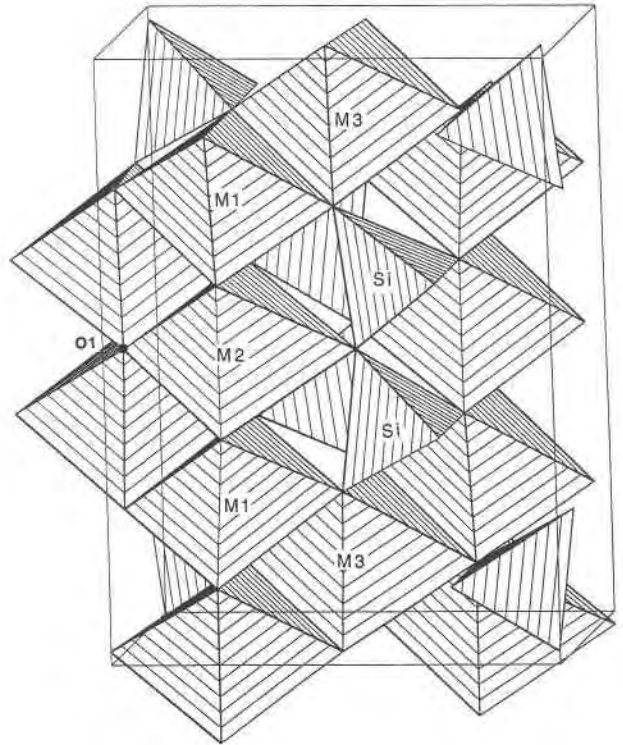

Fig. 1. β-Mg₂SiO₄ structure, perspective a-axis projection, c horizontal. The Si₂O₇ groups are clearly shown. This is a sorosilicate, not an orthosilicate or spinel. The O1 position (labeled) does not bond to Si and thus may be a potential site for water in the lower part of the upper mantle.

remained in this material and aided the synthesis not only by catalyzing reaction but also by entering and stabilizing the β structure. The crystal analyzed by Horiuchi and Sawamoto (1981) had been synthesized from (presumably) dry forsterite starting material, but their analysis showed a marginally significant less-than-full (97%) occupancy of M1 by Mg. Taken together, these lines of evidence support the hypothesis that hydroxyl is a possible substituent in the O1 site of β-Mg₂SiO₄ and that if charge balance were maintained by partial M-site vacancy, this structure might contain significant quantities of hydroxyl in the lower part of the upper mantle.

Liu (1985) reported that the presence of water suppresses the appearance of β-Mg₂SiO₄ in experiments at temperatures of 700 to 750 °C and pressures up to 13.5 GPa. Such temperatures are appropriate for simulation of a cool subducting slab, but in order for these experiments to be considered negative evidence for substitution of hydroxyl in β-Mg₂SiO₄, additional experiments would be required in the temperature range of 1250 to 1600 °C.

Assuming that charge balance is possible by partial M1 vacancy, electrostatic potentials of the sites in β-Mg₂SiO₄ were recalculated with a charge of 1.0 on M1 and a charge of −1.0 on O1 to simulate half-occupancy of M1 by Mg and occupancy of O1 by hydroxyl, respectively. The resulting value for O1 (17.7 V, Table 1) is approximately

2σ above the mean for the other OH and F positions given in Table 1. However, its value when modeled with a charge of -2 was more than 4σ below those of other nonhydroxyl oxygens (Table 2). Thus, although the Pauling bond-strength sum and electrostatic potentials of this site are somewhat higher than those of other hydroxyls, this site more resembles a hydroxyl site than an oxygen site in its electrostatic potential.

DISCUSSION

There appear to be strong crystal-chemical arguments in favor of partial hydroxyl substitution in O1 of β-Mg₂SiO₄. If it can be demonstrated experimentally that this does occur, there would be substantial consequences for geophysical and geochemical models of the upper mantle. The α–β transition in Mg₂SiO₄ has been postulated as the major cause of the 400-km seismic-velocity discontinuity (Ringwood, 1970, 1975; Anderson, 1970; Liu, 1979; Bina and Wood, 1987). The possibility of hydroxyl-bearing β-Mg₂SiO₄ introduces an additional degree of freedom into the thermochemistry of the reaction and the phase diagram for (Mg,Fe)₂SiO₄. Intuitively, one would expect the effect to be to spread the reaction over a larger reaction interval than that calculated by Bina and Wood (1987), but this would require experimental determination. Also, the stability field for β-Mg₂SiO₄ in a hydrous mantle might be considerably larger than in a completely dry mantle. Further, in an upward convection current in a hydrous mantle, it might be possible to generate partial melts on crossing from the β to the α stability field. If present, such melts would cause reduced seismic velocities above 400 km in upward convection currents. Indeed, reduced velocities have been noted in such regions (Nataf et al., 1986; Anderson, 1987).

It should be possible to detect hydroxyl in β-Mg₂SiO₄ by IR or Raman spectroscopy. Raman spectra for the phase have been published (Akaogi et al., 1984; McMillan and Akaogi, 1987). The latter spectrum is not inconsistent with hydroxyl, but data were not collected in the critical wavelength region to confirm the presence of hydroxyl. Inasmuch as IR or Raman measurements of existing samples in the critical wavelength region should be a fairly straightforward experiment, they should be pursued. Perhaps more diagnostic, however, would be spectroscopic measurements on samples synthesized under hydrous conditions at temperatures in excess of 1200 °C. If hydroxyl is detected, extensive experimental and thermochemical data will be required to constrain the effects of water on the stability of this phase.

CONCLUSIONS

Electrostatic and crystal-chemical calculations indicate that of the silicate and oxide phases generally believed to compose the mantle of the Earth, the O1 site in β-Mg₂SiO₄ is the most likely to contain significant amounts of hydroxyl. If it is possible for charge balance to be maintained in this structure by partial M-site vacancy, it may be possible for this structure to accommodate sufficient

hydroxyl to have a major effect on the phase relations in an olivine-rich upper mantle. Raman or IR spectroscopic methods should be capable of detecting this substitution in samples synthesized under hydrous conditions. If hydroxyl is detected in β-Mg₂SiO₄, careful experimental studies will be required to outline the possible effects of water on the stability of this phase in the (Mg,Fe)₂SiO₄ system.

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