LETTER

Crystal structure of superhydrous B, a hydrous magnesium silicate synthesized at 1400 °C and 20 GPa

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ABSTRACT

A unique magnesium silicate, $Mg_{10}Si_3O_{14}(OH)_4$, is the first hydrous phase found to be stable at 20 GPa and 1400 °C. Superhydrous B crystallizes in the orthorhombic space group *Pnnm* with lattice parameters $a = 5.0894(6)$ Å, $b = 13.968(7)$ Å, and $c = 8.6956(2)$ Å. Examination of the crystal structure indicates that superhydrous B is part of a series related by crystallographic shear performed on an olivine-type structure. The series includes previously described phases, B and anhydrous B, which are stable at lower temperatures and pressures. Superhydrous B, which would exist between 500 and 600 km, provides a possible vehicle for transport of H_2O to this depth in the Earth. The dehydration of this material may have far-reaching implications for mantle processes.

INTRODUCTION

The presence of hydrous magnesium silicates in the Earth's mantle can have a profound influence on its physical characteristics. Most studies of mantle mineralogy have focused on dry systems; however, the recent discovery that hydrous materials are stable to extremely high temperatures and pressures requires some reevaluation of our current understanding of mantle processes and phase relations. Hydrous magnesium silicates were first investigated by Ringwood and Major (1967) in the *P-T* range 10–18 GPa and 600–1100 °C. More recent work expanding on stability relations in the $MgO-SiO_2-H_2O$ system is described by Gasparik (1991; and personal communication, 1992). Indeed, a number of researchers present models for the Earth that are consistent with up to 2.0 wt% H_2O in the mantle (Tyburczy et al., 1991; Bell and Rossman, 1992; Abe and Matsui, 1986; Fukai and Suzuki, 1986).

One of the more puzzling questions concerning mantle processes has been the origin of deep-focus earthquakes. Although conventional theories of brittle fracture and frictional sliding are inconsistent with earthquakes occurring deeper than ~100 km (Scholz, 1990; Griggs and Baker, 1969), deep-focus earthquakes occur quite frequently, particularly under convergent plate boundaries (Frohlich, 1989). The dehydration of H_2O-bearing phases at great depth within the mantle, possibly contained within the subducting slab, may trigger these earthquakes (Raleigh and Paterson, 1965). Previous investigations of serpentine suggest that acoustic emissions, interpreted as microearthquakes, are produced when serpentine dehydrates (Meade and Jeanloz, 1991). Since the dehydration

occurs at relatively low pressures and temperatures, this reaction may generate earthquakes in serpentine-rich portions of a downward slab as it passes through depths of 200–300 km. By analogy, H_2O-bearing phases that are stable to higher temperatures and pressures will dehydrate at greater depth in the mantle, potentially producing earthquakes between 500 and 700 km.

A new material, designated superhydrous B (Shy-B), was first documented by Gasparik (1990). Subsequent experimental work (Gasparik, personal communication, 1992) found the assemblage Shy-B + stishovite to be stable between 15 and 23 GPa at temperatures of 800–1400 °C. Because it is compositionally within the range of mantle materials and it has the potential to be a repository for H_2O to extraordinary depths within the mantle, the physical properties of this unusual material are of great interest. The inadvertent synthesis of high-quality single crystals of Shy-B provided an opportunity to study its crystal chemical relationship with the other B phases.

EXPERIMENTAL DETAILS

Superhydrous B crystals were synthesized at 20 GPa and 1400 °C in the uniaxial split-sphere apparatus (USSA-2000) (Pacalo and Gasparik, 1990, and references therein). The starting material was an oxide mix of $Mg(OH)_2$ and SiO_2 with a molar ratio of 2/1; the bulk composition was equivalent to olivine + H_2O. Excess H_2O was added to the sample to act as a mineralizer for the growth of crystals. The experimental product consisted of clear, blocky crystals of Shy-B up to 0.4 mm on edge, as well as some fine-grained stishovite and glass. Electron probe microanalysis yielded a crystal composition

TABLE 2. Fractional coordinates (×10⁴) and isotropic thermal parameters (Å²)

Atom	Site	x	y	z	B_{iso}*
Si1	2d	5000	0	0	0.35(1)**
Si2	4g	4860.1(8)	3765.2(3)	0	0.29(1)
Mg1	4g	1694.1(10)	1735.1(4)	0	0.54(1)
Mg2	8h	1583.1(7)	3234.6(3)	3238.0(4)	0.53(0)
Mg3	4e	5000	5000	3212.7(6)	0.40(1)
Mg4	4f	5000	0	3418.9(6)	0.43(1)
O1	8h	3322.1(14)	4131.8(5)	1561.2(8)	0.46(1)
O2	4g	4930.9(22)	2592.3(7)	0	0.43(2)
O3	4g	7914.1(21)	4145.0(7)	0	0.47(2)
O4	8h	3564.0(14)	730.7(5)	1446.4(8)	0.41(1)
O5	8h	−174.5(18)	2518.5(5)	1592.0(8)	0.61(1)
O6	8h	1956.8(20)	−792.1(7)	0	0.51(2)
H1	8h	−769(37)	3026(13)	1085(17)	4.3(4)

Note: MoKα radiation, λ = 0.7107 Å; ω/2θ scans from 3° ≤ 2θ ≤ 60°; a = 5.0894(6) Å, b = 13.968(7) Å, c = 8.6956(2) Å, V_{cell} = 618.16(10) Å³. Space group $Pnnm$, Z = 2, formula weight = 619.4 g, ρ_{calc} = 3.327 g/cm³. The μ_i = 9.940 cm⁻¹, two data octants measured, merge R = 1.3%. Full matrix least squares refinement on F with R = 0.025, R_w = 0.021 where the weighting factor $w = [\sigma_i^2 + 0.0008 \ I^2]^{-1/2}$ for 898 unique data (I > 0); error of fit = 1.48 with anisotropic thermal parameters for Si, Mg, and O.

* Equivalent isotropic thermal parameters (Å) for the Si, Mg, and O sites; the H site was refined isotropically.

** Numbers in parentheses are estimated standard deviations in the last quoted decimal place.

TABLE 3. Selected interatomic distances (Å)

Si1-O4	1.7770(7)*	Mg1-O2	2.036(1)
Si1-O6	1.903(1)**	Mg1-O4	2.1108(8)**
Si2-O1	1.6486(8)**	Mg1-O5	2.0045(8)**
Si2-O2	1.639(1)	Mg1-O6ᵍ	2.277(1)
Si2-O3	1.642(1)	Mg2-O1	2.1166(8)
Mg1-Mg2ᵈ	2.9224(7)†	Mg2-O2ⁱ	2.0948(8)
Mg1-Mg2ᵉ	3.0192(7)†	Mg2-O4ᶜ	2.1272(8)
Mg1-Mg3ᶠ	3.0054(5)*	Mg2-O5	1.9619(8)
Mg2-Mg2ʰ	3.0643(7)	Mg2-O5ᵇ	1.9625(9)
Mg2-Mg3	3.0175(4)†	Mg2-O6ʲ	2.1790(8)
Mg2-Mg4ᶜ	2.9675(5)†	Mg3-O1	2.0644(8)**
Mg3-Mg4ᵇ	2.9135(6)*	Mg3-O4ᵇ	2.1023(8)**
Mg4-Mg4ʰ	2.750(1)	Mg3-O6ʲ	2.1521(8)**
O5-H1	0.888(18)	Mg4-O1ᵇ	2.0807(8)**
O5-H1ᵃ	2.452(18)	Mg4-O3ᵏ	2.1079(9)**
O3 . . . H1ˡ	1.945(18)	Mg4-O4	2.1256(8)**

Note: Symmetry operation codes for Table 3. Numbers in parentheses are estimated standard deviations in the last quoted decimal place. a = x, y, −z; b = ½ + x, ½ − y, ½ − z; c = −½ + x, ½ − y, ½ − z; d = ½ + x, ½ − y, −½ + z; e = −½ + x, ½ − y, −½ + z; f = ½ − x, −½ + y, −½ + z; g = −x, −y, −z; h = x, y, 1 − z; i = −½ + x, ½ − y, ½ + z; j = ½ − x, ½ + y, ½ + z; k = ¾ − x, −½ + y, ½ + z; l = 1 + x, y, z.

* Bond multiplicity = 4.
** Bond multiplicity = 2.
† Bond multiplicity = 3.

of $Mg_{10}Si_3O_{14}(OH)_4$, matching the composition first published for Shy-B (Gasparik, 1990).

Initial data from X-ray precession photographs indicated that Shy-B possessed orthorhombic symmetry, extinction symbol Pnn-. X-ray intensity data (2097 reflections) were obtained with a Huber diffractometer using a pyrolytic graphite monochromater; data were corrected for Lorentz and polarization effects, but not for absorption. The structure factors were averaged in Laue group *mmm,* resulting in a set of 898 unique structure factors with I > 0 (Table 1).[1] The cell parameters were determined from 25 reflections with 28° < 2θ < 35° (Table 2). A comparison of the unit-cell parameters with those of known phases confirmed the material was of a new structure type. Structure solution was initiated in space group $Pnnm$ and was solved using direct methods. The H position was located using a Fourier difference map. Refinement of a model with 85 variable parameters, including anisotropic thermal parameters for all but the H atoms, quickly converged to the values given in Table 2. Selected interatomic distances are listed in Table 3.

DISCUSSION

The crystal structure of Shy-B is closely related to the other two members of the B series, anhydrous phase B (Anhy-B) and phase B (B) (Finger et al., 1991). All three consist of the ordered intergrowth of two structural elements along the **b**-axial direction (Fig. 1a). Double O-T layers, containing octahedrally (O) coordinated Mg and tetrahedrally (T) coordinated Si alternate along **b** with O layers, containing both Mg and Si in octahedral coordination, but with no [4]Si (Fig. 1). Fully one-third of the Si atoms in the Shy-B structure are in octahedral coordination.

Compositional variation among the B series, specifically the higher H_2O content and increasing Mg/Si ratio of Shy-B, is achieved by rearrangement within the O-T and O layers. The structure of the O-T layer in all three materials is related to that of olivine by crystallographic shear along a direction subparallel to the [010] direction of olivine (Fig. 2). In Figure 2a, the (100) layer of olivine is shown; a similar layer exists in the structure of Anhy-B. Successive crystallographic shear within this layer produces the layer observed in phase B (Fig. 2b). If the density of shear is doubled, the layer found in Shy-B is obtained (Fig. 2c). H atoms are contained between the O-T layers (Fig. 1c) and are bonded to O atoms that coordinate only to Mg. As expected from simple electrostatic arguments, the [6]Si⁴⁺ in the O layer (Fig. 1b) are surrounded by Mg²⁺-centered octahedra; none of the structures in the B series (Finger et al., 1991) contain adjacent [6]Si⁴⁺. The strict segregation of [4]Si⁴⁺ and [6]Si⁴⁺ into distinct structural elements appears to be a general feature of the B series of Earth materials.

CONCLUSIONS

Superhydrous B is less dense (3.327 g/cm³) than the other B phases (B = 3.368 g/cm³, Anhy-B = 3.435 g/cm³; Finger et al., 1991), presumably because of its higher H_2O content and higher Mg/Si ratio. However, given a bulk mantle composed of equal amounts of forsterite and en-
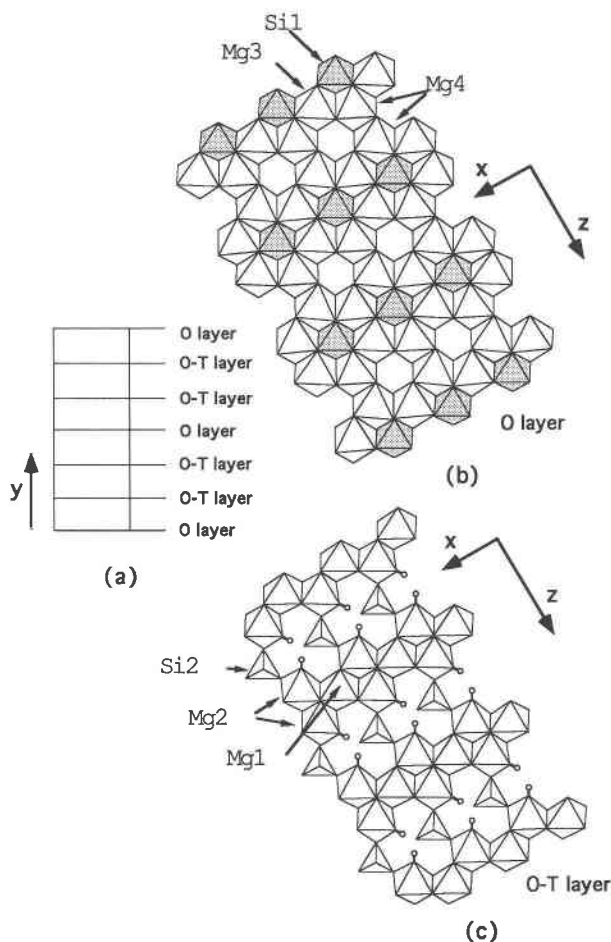
(a)

(b)

(c)

Fig. 1. (a) Schematic representation of the stacking of octahedral (O) and mixed octahedral-tetrahedral (O-T) layers in Shy-B along the **b**-axial direction. This same stacking sequence is observed in Anhy-B and B. The two distinct layers observed in Shy-B are (b) a defect rocksalt-type layer containing only [6]Mg and [6]Si, shown shaded, and (c) a layer with [4]Si and [6]Mg. The defects in the O-layer (b) are overlain by the tetrahedra in the O-T layer (c). Small circles in **c** represent H atoms.

statite, with an atomic ratio Mg/Si = 1.5 (Liu, 1987), the stable assemblage at relevant mantle depths, Shy-B + $MgSiO_3$ (ilmenite) + SiO_2 (stishovite) (Gasparik, personal communication, 1992), is more dense than an assemblage of B + SiO_2 (stishovite).

Mixing of the three types of layers found in the B series (Fig. 2) in the framework of the stacking sequence shown in Figure 1a may lead to related compositions (Finger and Prewitt, 1989). The discovery and characterization of this series of materials emphasizes the necessity for a careful evaluation of hydrous phase relations along all portions of the geotherm. The sequence of transitions linking low-pressure hydrous phases to these newly discovered high-pressure hydrous phases must be established before the hypothesis that deep-focus earthquakes are driven by the dehydration of H_2O-bearing phases can be tested.
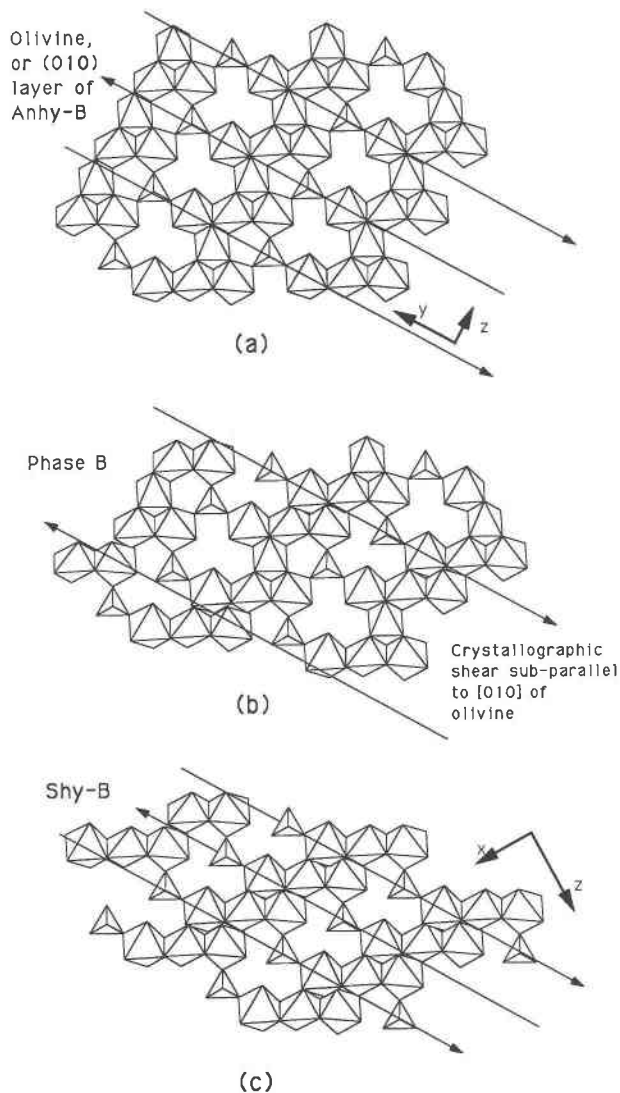

(a)

(b)

(c)

Fig. 2. Polyhedral representation of the relationship between olivine and the O-T layers found in the B series of materials. The layer found in Anhy-B closely resembles the (100) plane of forsterite, Mg_2SiO_4, the Mg end-member of the olivine series. The (001) shear planes are shown as arrowed lines (a); the direction of shear is subparallel to the [010] direction of olivine. If forsterite is sheared along every second one of these planes (b), the layer found in phase B results; shear on every plane (c) produces the O-T layer found in Shy-B.

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