Papers from the GEOPHYSICAL LABORATORY
Carnegie Institution of Washington NO. 2144

Reprinted from Nature, Vol. 341, No. 6238, pp. 140-142, 14th September, 1989

Crystal chemistry of phase B and an anhydrous analogue: implications for water storage in the upper mantle

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WATER locked in mineral phases within the Earth's mantle may be as significant for the development of life as water now found at the planet's surface. The Earth's original hydrosphere probably would not have survived a collision with a Mars-sized object, such as may have formed the Moon[1]. The water now on the surface could have been replenished by further impacts of smaller planetesimals; however, at least a portion could have been stored in minerals deep in the mantle being released gradually through volcanic eruptions. This mechanism requires a stable high-pressure phase able to store water under mantle conditions. Of the several hydrous phases studied in the past, the material known as phase B has the highest density and is the only known hydrous form stable at pressures corresponding to depths of 400–500 km (refs 2, 3). Although phase B has been known for over twenty years, its crystal structure and crystal chemistry have remained an unsolved problem. Here we describe the crystal structures of phase B ($Mg_{12}Si_4O_{19}(OH)_2$) and a chemically and structurally similar anhydrous form, AnhB ($Mg_{14}Si_5O_{24}$). These structures contain silicon in both fourfold and sixfold coordination; the silicon octahedra share all twelve edges with magnesium octahedra in a unique thirteen-cation cluster. Description of the structures of phases AnhB and B requires 18 and 40 atoms, respectively, demonstrating that high-pressure phases can have very complicated crystal structures. The multitude of octahedral sites in these phases could lead to rather complicated fractionation behaviour during solid–solid or solid–liquid transitions in the presence of other octahedrally coordinated ions such as Al, Fe, Ti and Mn.

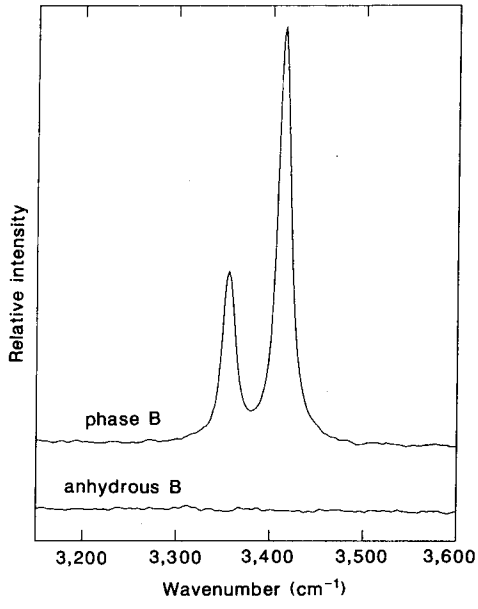

FIG. 1 Raman spectra of phase B (top curve) and anhydrous phase B (bottom curve) measured with 457.9-nm laser excitation (~25 mW) and 5-cm^{-1} resolution. The peaks in the phase B spectrum, which arise from OH-stretching vibrations, appear at 3,414 and 3,356 cm^{-1}, frequencies similar to those found[4] in the infrared absorption spectrum.

The stability of high-pressure hydrous phases has been known since the report[2] of preliminary data for what were named phases A, B and C. Phase B, which formed from gels with Mg/Si = 3 at pressures >11 GPa, had the highest density of the new forms and seemed to be an interesting possibility for the mantle, whether hydrous or not. The determination[3–5] of the unit cell, space group and infrared spectra of synthesized crystals of phase B confirmed the presence of hydroxyl groups; the structure, however, was not determined. The hydrous phase B was reported[6,7] to be the second liquidus phase for natural lherzolite and synthetic compositions that were heated at a pressure of 20 GPa. No water was added to the capsules in these experiments and the hydrous phase seemed to persist at very high temperatures even though water usually enters the melt at relatively low temperature. Electron-microprobe results suggest[8] that this high-temperature phase is actually anhydrous.

Single crystals of phase B were synthesized in a split-sphere anvil apparatus (USSA-2000) starting from a gel with Mg/Si = 3. The charge was heated to 1,200 °C at 12 GPa and cycled between 1,200 and 1,300 °C, a procedure that produced the largest grain size. Crystals selected from the run products have a monoclinic cell (see Table 1) similar to that reported in ref. 5. Some crystals demonstrate twinning, which we believe to be the result of a twofold operator parallel to [001], but, most did not. In addition, high-resolution transmission-electron-microscope photographs did not indicate the presence of stacking faults. The unit-cell geometry and space group are highly suggestive of a structure with some layers similar to that of MgO and a six-layer stacking sequence. In such a structure, the oxygen substructure would have cubic closest-packing arrangement, a situation confirmed by a Patterson synthesis. Because of this pseudosymmetry, a solution was not obtained by the standard direct methods.

Single crystals of the new phase, AnhB, were grown from a starting material consisting of synthetic forsterite that had been dried at 1,000 °C in argon immediately before the experiment; run conditions were 2,380 °C and 16.5 GPa for 2 h. The new phase formed large single crystals at the centre of the capsule, with quenched crystals in the hot end and β-Mg_2SiO_4 in the colder portion of the charge. Phase AnhB was formed by incongruent melting of β-Mg_2SiO_4 to AnhB plus melt, which segregated during the experiment. Electron-microprobe analysis gave an atomic Mg/Si ratio of 2.81 (9 analyses) and a total close to 100%. The lattice (see Table 1) also indicates a six-layer stacking sequence. Although this structure has pseudosymmetry, the solution was obtained by routine direct methods[9] and difference electron-density calculations; the phase is isostructural[10] with $Mg_{14}Ge_5O_{24}$. We have revised the choice of orthorhombic axes, however, to maintain the similarities between phases B and AnhB. To test for substitution of $Mg+H_2$ for Si, valence-bond sums[11] were calculated. All oxygen ions were fully bonded; furthermore, the Raman spectra (Fig. 1) showed none of the features associated with the presence of OH groups. An *a*–*c* projection of the structure is shown in Fig. 2. Not only is this the phase identified in ref. 8 but it is probably the high-temperature form identified as phase B in refs 6, 7. In addition, phase B has been found[12] to break down at high pressure at ~1,000 °C; above 22 GPa, the quenched sample consisted of one or more unknown phases. Phase AnhB, with some Fe substitution for Mg, would explain two of the three strongest X-ray lines found in that study. Another, as yet unidentified, phase is required to account for the third diffraction line. It is probable, however, that this phase is produced in a reaction that yields free water as a product.

Using the structure model for AnhB we obtained the solution of the hydrous form. The Raman spectrum (Fig. 1) indicates two distinct OH groups, which is consistent with the calculated

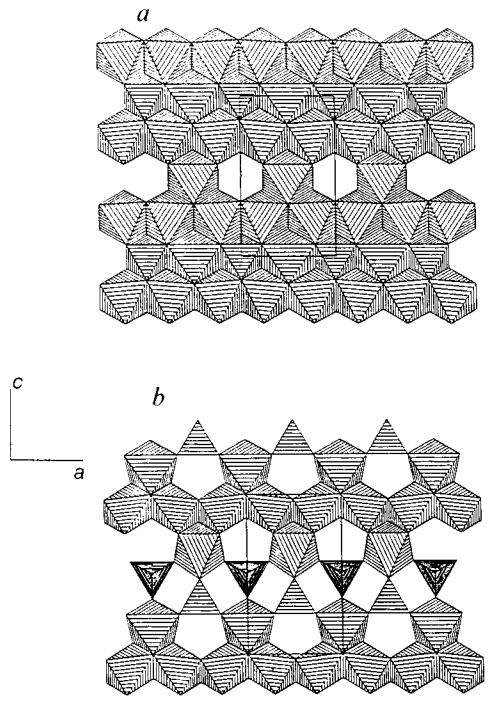

FIG. 2 Polyhedral[20] projection of the structure of $^{VI}Mg_{14}{}^{VI}Si_1{}^{IV}Si_4O_{24}$ (AnhB) viewed parallel to (010). (Roman-numeral superscripts indicate the coordination). Structure consists of two types of layers repeated by symmetry. Magnesium is in six-fold coordination as in olivine or spinel; however, silicon is in mixed coordination. *a*, Defect (Mg, Si)O layer, with $-0.12 \leq y \leq 0.12$, similar to that of spinel[21], but with fewer vacancies and with a smaller Si octahedron at the origin. There are two layers of this type per unit cell. *b*, Layer with $-0.30 \leq y \leq -0.07$ containing Mg octahedra and Si tetrahedra. There are four layers of this type per unit cell. The Si octahedron in *a* is capped by a cluster of Mg octahedra; thus all 12 edges of the Si octahedron are shared with Mg octahedra. The Si tetrahedra are placed directly over the hole in the first layer; thus, octahedra and tetrahedra share corners as in spinel rather than olivine; this layer is identical, however, to *b*–*c* layers of the olivine structure.

TABLE 1 Equivalent isotropic temperature factors and mean bond distances for cations of phases AnhB and B

	AnhB		B	
	B_{eq}	Mean M–O	B_{eq}	Mean M–O
Si 1	0.33 (2)*	1.804	0.26 (1)	1.816
Si 2	0.34 (1)	1.657	0.34 (2)	1.659
Si 3	0.35 (1)	1.625	0.35 (2)	1.655
Si 4			0.39 (2)	1.624
Mg 1	0.47 (2)	2.097	0.48 (2)	2.090
Mg 2	0.49 (2)	2.110	0.50 (2)	2.101
Mg 3	0.48 (1)	2.106	0.56 (3)	2.085
Mg 4	0.46 (1)	2.093	0.49 (2)	2.094
Mg 5	0.44 (1)	2.076	0.46 (2)	2.092
Mg 6	0.46 (1)	2.088	0.43 (2)	2.086
Mg 7			0.46 (2)	2.086
Mg 8			0.45 (2)	2.114
Mg 9			0.47 (2)	2.084
Mg 10			0.49 (2)	2.089
Mg 11			0.47 (2)	2.091
Mg 12			0.49 (2)	2.087
Mg 13			0.52 (3)	2.128

Diffraction experiments with Rigaku AFC-5 diffractometer, rotating-anode generator, Mo $K\alpha_1$ radiation, graphite monochromator, $\lambda = 0.7093$ Å, ω step scans to $2\theta = 60°$, ambient pressure and temperature. Phase AnhB: $a = 5.868(1)$ Å; $b = 14.178(1)$ Å; $c = 10.048(1)$ Å; $V_{cell} = 835.9$ Å^3. Space group *Pmcb*; $Z = 2$; relative molecular mass = 864.8; $\rho_{calc} = 3.435$ g cm^{-3}; linear absorption coefficient $\mu_l = 10.8$ cm^{-1}; range of transmission factors = 0.81–0.92; two octants measured; internal agreement 2.5%. Residuals $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.040$, $R_w = \Sigma\sigma_F^{-2}(F_o - F_c)^2/\Sigma\sigma_F^{-2}F_o^2 = 0.025$ for all 1,337 independent data where F_o is the observed structure factor and F_c the calculated structure factor, $R = 0.029$, $R_w = 0.024$ for 1,132 data with $F_o > 2\sigma_F$; goodness of fit = 0.9 for anisotropic temperature factors. Phase B: $a = 10.588(2)$ Å; $b = 14.097(1)$ Å; $c = 10.073(1)$ Å; $\beta = 104.10(3)°$; $V_{cell} = 1{,}458.4(3)$ Å^3. Space group $P2_1/c$; $Z = 4$; relative molecular mass = 742.1; $\rho_{calc} = 3.368$ g cm^{-3}; $\mu_l = 10.3$ cm^{-1}; Range of transmission factors = 0.87–0.94; hemisphere of reciprocal space measured; internal agreement 3.5%. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.080$, $R_w = \Sigma\sigma_F^{-2}(F_o - F_c)^2/\Sigma\sigma_F^{-2}F_o^2 = 0.041$ for all 4,263 independent data; $R = 0.039$, $R_w = 0.056$ for 3,254 data with $F_o > 2\sigma_F$; goodness of fit = 1.0 for anisotropic temperature factors.

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

valence sums[11]. These values are 1.2 and 1.3, respectively, compared to a value of 2.0 for a fully bonded ion. A nearby oxygen had a value of 1.6 indicating an asymmetric hydrogen bond. Trial positions were generated from these calculations and the parameters of all atoms were refined, using anisotropic thermal models for all non-hydrogen atoms. Figure 3 is an *a*–*c* projection of the structure. The hydrogen atoms lie 0.8–0.9 Å from the oxygen associated with a silicon tetrahedron.

The high density of these structures arises, in part, from total edge sharing between the silicon octahedron and the surrounding magnesium octahedra, which forms a thirteen-cation cluster. Unlike the lower-pressure forms olivine, clinohumite, humite, chondrodite and norbergite[13], and the hydrous high-pressure form, phase A[14], the new structures do not contain shared edges between tetrahedra and octahedra. In addition, only phases B and AnhB have silicon in octahedral coordination.

Other high-pressure forms of magnesium silicate may exist. The germanate form of AnhB has been described[15] as a member of a homologous series containing variable ratios of olivine and defect rock-salt layers (in AnhB this ratio is 2:1). $Mg_{10}Ge_3O_{16}$, a stoichiometry that might occur in the silicate system has also been reported[16]. As shown in Fig. 3, phase B can be described as a 2:1 mixture of humite and defect rock salt. It is probable that the 1:1 form, which would have a hexagonal close-packed oxygen array with composition $Mg_{17}Si_5O_{26}(OH)_2$, also exists. Other series based on clinohumite, chondrodite or norbergite layers mixed with the appropriate octahedral layers can be imagined. In addition as phase B can be related to AnhB by a 'shearing' parallel to the *c* axis, one can propose other forms involving different slab widths or 'shear' offsets leading to further structures or complex intergrowths such as those found in the biopyriboles[17].

This study illustrates the utility of a large-volume high-pressure apparatus in growing single crystals of high-pressure phases that are suitable for crystal structure determination. This is important because the solution of these complicated structures would not be possible with powder X-ray diffraction methods. We note that very complex crystal structures can exist at high pressure in contradiction to the standard assumptions. For example, it has been proposed[22] that the lower mantle is composed predominately of simple orthorhombic perovskites over the entire *P*–*T* range. Although there is no evidence to refute this claim, we emphasize that it has not yet been confirmed by *in situ* simultaneous high-pressure and high-temperature measurements.

This study also has implications regarding the storage and release of water in the upper mantle. Although these phases are more magnesian than any possible mantle model, mixture with stishovite would permit any desired Mg:Si value, with a high density. The assemblage B + stishovite with Mg/Si = 1.5 has 1.8% H_2O and an atmospheric-pressure density of 3.554, which is 9% denser than A + spinel + clinoenstatite of the same composition and 8% denser than clinohumite + stishovite[18]. Phase B is stable to 22 GPa at 1,000 °C (ref. 12), but transforms to AnhB at higher temperatures according to our interpretation of the data in ref. 6. This reaction, which might be B + spinel →

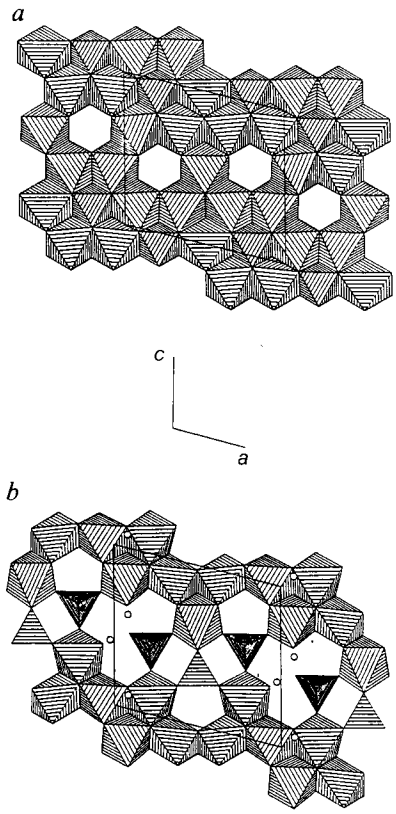

FIG. 3 Polyhedral projection of the structure of $^{VI}Mg_{12}{}^{VI}Si_1{}^{IV}Si_3O_{19}(OH)_2$ (Phase B) viewed parallel to (010). (Roman-numeral superscripts indicate coordination.) This structure also has a two-layer form. *a*, The defect (Mg, Si)O layer, with $-0.12 \leq y \leq 0.12$, has a central vertical section identical to that of Fig. 2*a*; however, there is a 'sheared' relationship between adjacent strips in the hydrous form. Note that the silicon octahedron is no longer located at the origin. *b*, Layer with $-0.30 \leq y \leq -0.07$ containing Mg octahedra, Si tetrahedra, and hydrogens indicated by small circles. This layer is identical to *b*-*c* layers of the humite structure.

$AnhB + H_2O$ or B + stishovite → $AnhB + H_2O$, could be a mechanism for storage and release of large volumes of water. A possible scenario is that during the early history of the mantle, a magma ocean might first crystallize garnet, then AnhB. On cooling in the presence of water, the reaction would proceed to the left, storing the water in the solids. The difficulty with this scenario is that the hydrous phase B has not been shown to be stable in realistic mantle compositions; its phase relations are little known. We believe that there has been insufficient water present in most experiments to stabilize hydrous phase B. Further work is certainly required to clarify details of the possible phase relations.

Even if high-pressure hydrous silicates were not involved in the formation of primordial surface water, there is circumstantial evidence for their importance in maintaining a hydrosphere. Those planets too small to stabilize phase B in their mantles (Moon, Mercury) are completely dry[1]. The roughly 20-GPa pressures at the core-mantle boundary of Mars would limit the volume of phase B and its surface water has not been replaced. Venus is more complicated. Phase B should be abundant but at a greater depth than on Earth. The quantity of water in the atmosphere will be affected by the efficiency of volcanism in tapping this source and by the extent to which atmospheric water is photodissociated and H_2 lost[19]. □

Received 5 June; accepted 8 August 1989.

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ACKNOWLEDGEMENTS. We thank D. Veblen for transmission-electron-microscope examinations of phase B. The synthesis of single crystals was performed in the Stony Brook High-Pressure Laboratory, which is jointly supported by NSF and the State University of New York, and the X-ray diffraction data were obtained at the Geophysical Laboratory, which is supported by NSF and by the Carnegie Institution of Washington.