

Are hydrous phases more compressible? Implications for high-velocity zones in the deep mantle

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SUMMARY

Raman studies of both anhydrous and hydrous α , β and γ phases of Mg_2SiO_4 provide us with evidence that some hydrous phases are less compressible than their anhydrous counterparts. This is contrary to the generally accepted view that all hydrous phases are more compressible than corresponding anhydrous phases. It is suggested that the inclusion of these hydrous phases, together with hydroxyl-clinohumite and phase D ($\text{MgSi}_2\text{H}_2\text{O}_6$), in some mantle material may be responsible for the high velocities observed in horizontal slabs lying above the 650-km discontinuity and in front of subducted slabs in the lower mantle.

Key words: compressibility, deep mantle, high-velocity zones, hydrous phases.

INTRODUCTION

It is widely accepted that H_2O is the most abundant fluid component on/in the Earth (e.g. Liu 1987). The occurrence of amphiboles and phlogopite as apparent primary constituents in peridotitic and eclogitic rocks and the P – T stability fields of these hydrous phases determined in laboratory studies suggest that these minerals exist in the shallow parts of the upper mantle.

Magnesium-rich olivine, or forsterite, is in general believed to be the most abundant mineral in the upper mantle. The possibility of the existence of water in limited amounts in certain oxygen lattice positions in the nominally anhydrous minerals, such as olivine and pyroxene, in upper-mantle conditions was speculated by Martin & Donnay (1972) based on crystallo-chemical considerations. These authors concluded that there is no need to appeal for new high-pressure hydrous phases in the mantle in order to accommodate H_2O . The OH concentration in nominally anhydrous upper-mantle minerals has been reviewed by Bell & Rossman (1992). Pyroxenes are the most hydrous and contain ~ 200 to 500 ppm H_2O by weight, and olivines and garnets contain ~ 1 to 50 ppm H_2O by weight. Thus, these very limited OH concentrations in nominally anhydrous upper-mantle minerals cannot be very significant to our understanding of the state of hydration of the mantle. On the other hand, Kohlstedt *et al.* (1996) recently found that San Carlos olivine can contain up to 0.15 wt per cent H_2O at 120 kbar and 1100°C in their hydrothermal annealing experiments. Although the H_2O contents of olivine in these high-pressure experiments are some two to three orders of magnitude higher than those found in natural olivine reviewed by Bell & Rossman (1992), these OH concentrations in nominally anhydrous upper-mantle minerals are still very limited.

Phase E ($\text{Mg}_{2.08}\text{Si}_{1.16}\text{H}_{3.20}\text{O}_6 \sim \text{Mg}_{2.17}\text{Si}_{1.01}\text{H}_{3.62}\text{O}_6$) has been observed in some mineral assemblages at temperature and pressure conditions relevant to the Earth's mantle (Kanzaki 1991; Ohtani *et al.* 1995). Although this material possesses features of brucite-

type units (Kudoh *et al.* 1993), it may be regarded as a hydrous forsterite containing 15–18 wt per cent H_2O from the viewpoint of chemistry and its Raman spectrum (Liu *et al.* 1997). Based on the results of shock experimental study of serpentine performed by Lange & Ahrens (1984) and assuming that the infalling materials contain ~ 0.3 wt per cent H_2O , Liu (1987) estimated that the Earth's interior might contain more than 5 times its present water content in the near-surface geochemical reservoirs (hydrosphere + crust). This is a rather conservative estimate if one considers that the water content of the A and B components proposed by Ringwood (1979) is one order of magnitude higher than 0.3 wt per cent. Thus, it is highly likely that most of the mantle olivine may convert to phase E.

Forsterite transforms to β - and γ -phases at high pressures and high temperatures, and the latter two phases are believed to be the most abundant minerals in the nominally dry transition zone. Considering the electrostatic potential and the polyhedral coordination in the β -phase structure, Smyth (1987) predicted that the O(1) sites in the β -phase may be replaced by OH^- . If all of the O(1) sites in the β -phase are assumed to be replaced by OH^- , the H_2O content in the hypothetical hydrous β -phase would be 3.3 wt per cent (Inoue *et al.* 1995). However, earlier experimental studies have found approximately 0.06 wt per cent (McMillan *et al.* 1991) and 0.32 wt per cent of H_2O (Young *et al.* 1993) in the β -phase. Depending upon the starting materials and experimental P – T conditions, Inoue (1994) and Inoue *et al.* (1995) have successfully synthesized several hydrous β -phases which contain up to 3.1 wt per cent H_2O . Recently, Kohlstedt *et al.* (1996) have synthesized the hydrous γ -phase which contains up to ~ 2.7 wt per cent H_2O , using San Carlos olivine. The pure magnesium hydrous γ -phase having an Mg/Si ratio of ~ 1.95 and H_2O content of ~ 2.2 wt per cent was later synthesized by Inoue *et al.* (1998).

Thus, the elastic properties of forsterite, β - and γ -phases and their corresponding hydrous phases are important, especially if these

phases are stable at the pressure and temperature conditions relevant to the mantle and there is sufficient H₂O in the mantle.

AVAILABLE EXPERIMENTAL DATA

The bulk modulus (B) of both the anhydrous and hydrous forsterite, β - and γ -phases mentioned above have been measured using different experimental techniques. Among them, the elastic properties of forsterite are the most reliably measured. The most recent measurement and all earlier data from ultrasonic studies give $B_{S,o}$ (adiabatic) = 1.29 ± 0.01 Mb for forsterite (e.g. Li *et al.* 1996). Compression measurements are less reliable because the reported values of $B_{T,o}$ (isothermal) depend on (1) the chosen equation of state, (2) the scheme of least-squares fitting and (3) the chosen value of B'_T (the first pressure derivative of B_T).

The available experimental data for all the phases mentioned above are listed in Table 1, together with other relevant information. It is obvious that values of B for all anhydrous phases have been better studied, though the difference between different studies is still much greater than the uncertainty commonly accepted. For instance, uncertainties in ultrasonic and Brillouin measurements of $B_{S,o}$ are commonly 1 per cent (Li *et al.* 1996; Weidner & Vaughan 1977), but the difference in $B_{S,o}$ for β -phase shown in Table 1 is ± 4 per cent. Only one measurement each for the hydrous phases was listed in Table 1. The elastic properties of phase E were studied by Bass *et al.* (1991) using Brillouin measurements. The results were reported only in a brief abstract. Although no value of $B_{S,o}$ was given, these authors suggested that phase E is more compressible than forsterite.

The compressional behaviour of the hydrous β -phase, on the other hand, was reported by Yusa & Inoue (1997) and the elastic moduli of the hydrous γ -phase was reported by Inoue *et al.* (1998). The values

of B reported by these studies are also given in Table 1. These results all showed that the hydrous phases are more compressible than their corresponding anhydrous phases (the bulk modulus is ~ 7.5 per cent different between the pair of anhydrous and hydrous β -phases and is ~ 19 per cent different between the pair of anhydrous and hydrous γ -phases). On the other hand, the fact that the values of bulk modulus are the same for the hydrous β - and γ -phases (both have values of 1.55 Mb) suggests that the results of these measurements are not entirely reliable. When the values of bulk sound velocity for these phases are calculated (see Table 4), it is astonishing to find that the bulk sound velocity for the hydrous β -phase is 2 per cent greater than that for the hydrous γ -phase calculated from these measurements. Yet, the latter is 4.2 per cent denser than the former and both contain about the same amount of H₂O (see Table 1).

BULK MODULUS AND VIBRATIONAL FREQUENCY

The bulk moduli and pressure derivatives of compounds having certain crystal structures (in particular, cubic) have been calculated from the data of vibrational frequencies of these compounds by Hofmeister (1991a,b). In comparison with the experimental results of these compounds, Hofmeister (1991a) concluded that the agreement between the calculations and experiments is within 7 per cent for certain solids, and is 'moderate' to 'poor' for others, depending upon the crystal structure. Calculation of the exact values of the bulk modulus from vibrational frequency data may be too ambitious. On the other hand, vibrational frequency data obtained at high pressures should provide information concerning the relative compression between related compounds such as the anhydrous and hydrous phases discussed above. This proposition is adopted in the present work.

Table 1. Ambient molar volume, density and bulk modulus of anhydrous and hydrous phases of α , β and γ phases of Mg₂SiO₄.

	Forsterite (α)	Phase E (Mg _{1.39} Si _{0.77} H _{2.13} O ₄)*
V (cm ³ mole ⁻¹)	43.79	42.58*
H ₂ O (wt per cent)	0	15.8
ρ (g cm ⁻³)	3.214	2.86
B_T (Mb)	1.28 (see Liu 1990)	?
B_S (Mb)	1.29 (see Li <i>et al.</i> 1996)	
	β -phase	Hydrous β -phase (Mg _{1.75} SiH _{0.5} O ₄)
V (cm ³ mole ⁻¹)	40.30	40.59
H ₂ O (wt per cent)	0	2.5 \pm 0.3
ρ (g cm ⁻³)	3.492	3.329
B_T (Mb)	1.66 (Mizukami <i>et al.</i> 1975) 1.67 (Tanaka <i>et al.</i> 1987) 1.60 (Hazen <i>et al.</i> 1990) 1.73 (Meng <i>et al.</i> 1993)	1.55 (Yusa & Inoue 1997)
B_S (Mb)	1.74 (Sawamoto <i>et al.</i> 1984) 1.77 (see Li <i>et al.</i> 1996) 1.63 (Gwanmesia <i>et al.</i> 1990) 1.70 (Li <i>et al.</i> 1996) 1.70 (Zha <i>et al.</i> 1997)	
	γ -phase	Hydrous γ -phase (Mg _{1.84} Si _{0.98} H _{0.42} O ₄)
V (cm ³ mole ⁻¹)	39.49	39.69
H ₂ O (wt per cent)	0	2.7 \pm 0.3
ρ (g cm ⁻³)	3.563	3.469
B_T (Mb)	1.83 (Meng <i>et al.</i> 1993)	1.51 (Yusa <i>et al.</i> 2000)**
B_S (Mb)	1.84 (Weidner <i>et al.</i> 1984)	1.55 (Inoue <i>et al.</i> 1998)

*The data for phase E determined by Kudoh *et al.* (1993) were recalculated assuming 4 oxygens in the formula.

** $B_T = 1.48$ Mb was reported by Yusa *et al.* (2000), who assumed $B'_o = 5$.

Table 2. Pressure dependency of Raman frequencies and derived values of B_o/B'_o for anhydrous and hydrous phases of α -, β - and γ -phases of Mg_2SiO_4 at ambient conditions.

$\Delta v_{o,i}$ cm^{-1}	$(\partial v_i/\partial P)_T$ $\text{cm}^{-1} \text{ kbar}^{-1}$	$1/(b_i/a_i - 2c_i/b_i)$ kbar	$\Delta v_{o,i}$ cm^{-1}	$(\partial v_i/\partial P)_T$ $\text{cm}^{-1} \text{ kbar}^{-1}$	$1/(b_i/a_i - 2c_i/b_i)$ kbar
Forsterite (α)			Phase E		
855	0.366	415	850	0.339	633
826	0.341	769	817	0.343	709
β -phase			Hydrous β -phase		
918	0.547	291	915	0.473	352
723	0.443	247	719	0.339	254
γ -phase			Hydrous γ -phase		
836	0.41	—	835	0.460	332
795	0.543	594	795	0.587	258
834	0.431	—			
796	0.551	1297			

Forsterite: Liu & Mernagh (1993); Phase E: Liu *et al.* (1997); β -phase: Liu *et al.* (1994); hydrous β -phase: The data given by Liu *et al.* (1998) were derived by linear equation. The original data were refitted by quadratic equations for the present work. γ -phase: 1st set data from Liu *et al.* (1994) and 2nd set from Chopelas *et al.* (1994); hydrous γ -phase: Liu *et al.* (2002).

Table 2 lists the Raman frequencies ($\Delta v_{o,i}$) and their pressure dependencies ($(\partial v_i/\partial P)_T$) for the most reliably measured Raman bands for both anhydrous and hydrous α -, β - and γ -phases. The pressure dependencies of the Raman bands for forsterite and phase E are nearly the same, with the latter being slightly less. This suggests that the compressibility between forsterite and phase E is nearly the same. The pressure dependencies of the Raman bands for anhydrous β -phase are in general greater than that of the corresponding Raman bands for the hydrous β -phase. This suggests that the hydrous β -phase is less compressible than the anhydrous β -phase. This seems to be in contradiction with the values of B for these two phases listed in Table 1. The pressure dependencies of the Raman bands for anhydrous γ -phase are slightly less than those of the corresponding Raman bands for the hydrous γ -phase. This would suggest that the hydrous γ -phase may be slightly more compressible than the anhydrous γ -phase, which is in line with the values of B for these two phases listed in Table 1. Thus, the compressional behaviour between the anhydrous and hydrous β -phases has an opposite relationship to that between the anhydrous and hydrous γ -phases on the basis of the measurement of Raman frequencies at high pressure.

This conclusion can be elucidated by a more rigorous derivation of the data. Nearly all the reported data for the pressure dependence of vibrational frequencies in the literature were derived by fitting frequency–pressure data using either a linear or a quadratic equation. The isothermal bulk modulus (B_T) of a material is related to its vibrational frequency through the following identity:

$$B_T = (\gamma_i)(v_i)/(dv_i/dP)_T \quad (1)$$

where v_i is the vibrational frequency for a given mode i , P and T are pressure and temperature, respectively, and γ_i is the mode Grüneisen parameter defined as

$$\gamma_i = -d \ln v_i / d \ln V \quad (2)$$

where V is volume. Although the linear treatment of the experimental data is statistically sound, it is theoretically unjustified as shown by Liu (2000).

If the pressure dependence was derived from a quadratic equation, then one has the following

$$v_i = a_i + b_i P + c_i P^2 \quad (3)$$

where a_i , b_i and c_i are constants in the quadratic equation. Assuming that γ_i remains constant over the pressure range studied, one finds that

$$B_{T,o} = \gamma_i a_i / b_i \quad (4)$$

and

$$B'_{T,o} = \gamma_i (1 - 2a_i c_i / b_i^2). \quad (5)$$

Therefore,

$$B_{T,o} / B'_{T,o} = 1 / (b_i / a_i - 2c_i / b_i). \quad (6)$$

Thus, the ratio of ($B_{T,o} / B'_{T,o}$) for a given material can be calculated directly from the parameters a_i , b_i and c_i in eq. (3), using eq. (6). The values of the pressure dependence for the various phases listed in Table 2 are equivalent to the values of b'_i s in eq. (3). Most dense mineral structures based on a close-packed array of oxygens have a similar value of $B'_{T,o}$ in the vicinity of 4, then the values of $1/(b_i/a_i - 2c_i/b_i)$ listed in Table 2 must represent the compressional behaviour of these materials. The conclusions reached by these data are exactly the same as those reached earlier by consideration of the pressure dependence alone. It should be noted that, with the exception of forsterite, all values of $B_{T,o}$ for the various phases listed in Table 1 were calculated from compression data by assuming $B'_{T,o} = 4$.

Only one assumption that γ_i remains constant over the pressure range studied is used in the above derivations. With the exception of α -quartz, γ_i for most silicates and oxides appears to remain constant over the pressure range studied (e.g. Sherman 1982; Liu & Wu 1992; Liu 1993).

Hydroxyl-clinohumite [$3\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH})_2$] may also be regarded as a hydrous phase of forsterite. Except for the presence of four extra OH vibrations in hydroxyl-clinohumite, the Raman spectra of forsterite and hydroxyl-clinohumite are nearly identical (Lin *et al.* 2000). The Raman data for these two phases are listed in Table 3. Because more Raman bands of these two phases were reliably determined, more data are given in Table 3. The values of $B_{T,o} / B'_{T,o}$ for hydroxyl-clinohumite are over-all greater than those for forsterite. Thus, it can be concluded that hydroxyl-clinohumite is less compressible than forsterite, even though both elastic and compressional measurements of hydroxyl-clinohumite are not available yet.

Table 3. Pressure dependency of Raman frequencies and derived values of B_o/B'_o for forsterite (α) and hydroxyl-clinohumite at ambient conditions.

Forsterite (α)			Hydroxyl-clinohumite		
$\Delta v_{o,i}$ cm ⁻¹	$(\partial v_i/\partial P)_T$ cm ⁻¹ kbar ⁻¹	$1/(b_i/a_i - 2c_i/b_i)$ kbar	$\Delta v_{o,i}$ cm ⁻¹	$(\partial v_i/\partial P)_T$ cm ⁻¹ kbar ⁻¹	$1/(b_i/a_i - 2c_i/b_i)$ kbar
964	0.7	224	965	0.541	—
—	—	—	936	0.369	628
921	—	—	929	0.323	977
—	—	—	900	0.424	278
883sh	0.387	217	873	—	—
866	0.388	360	—	—	—
855	0.366	415	857	0.319	765
839	0.377	330	839	0.290	638
826	0.341	769	826	0.293	849
—	—	—	764	0.302	319
—	—	—	738	0.236	895
610	0.325	480	604	0.301	—
585	—	—	584	0.236	—
434	0.617	214	429	0.556	375
—	—	—	331	0.484	318
Average 376 ± 187			Average 604 ± 265		

Thus, in short, the high-pressure Raman data would lead this author to conclude that not all hydrous phases are more compressible than their corresponding anhydrous phases.

GEOPHYSICAL IMPLICATIONS

A range of seismological evidence shows that, in addition to the inclined slabs, high velocities (in particular V_p) also exist either in the overlying upper mantle along the 650-km seismic discontinuity or in the lower mantle in front of some subducted slabs (e.g. van der Hilst *et al.* 1991, 1997, and references therein). This observation has so far been interpreted to imply that these high velocities are due to the extension of the cold slabs either deflected at the 650-km seismic discontinuity or penetrated into the lower mantle (e.g. van der Hilst & Karason 1999) and that old, cold slabs might also pile up on the mantle-core boundary to form the D'' zone (e.g. Lay 1994).

If cold slabs of subducted oceanic lithosphere are indeed deflected at the 650-km seismic discontinuity or 'sank' (this is probably the wrong word to use here because it implies that slabs are more dense than the surrounding mantle, see later discussion) deep into the lower mantle as implied by seismological studies, it would be important to know what materials are in these cold slabs. In brief, typical oceanic lithosphere comprises an upper layer of basalt with a thickness of about 7 km underlain by a layer of harzburgite and peridotite (e.g. Green *et al.* 1979). Thus, the most abundant mineral phase in subducted slabs is still olivine, or forsterite, the same as in the upper mantle, and the whole subducted body is cooler than the surrounding mantle. The intermediate and deep-focus earthquakes occurring in subducted oceanic lithosphere between 150 and 660 km are attributed to phase transformations taking place in the various metastable mineral phases which make up the subducted oceanic lithosphere (e.g. Liu 1983; Kirby *et al.* 1991; Meade & Jeanloz 1991; Kao & Liu 1995). Decomposition of metastable alumina-rich pyroxene to alumina-poor pyroxene and majorite garnet was proposed to generate the double seismic zones observed between 70 and 200 km by Kao & Liu (1995). Deep double seismic zones observed between 350 and 460 km were attributed to the transformation of metastable olivine to β -phase or spinel (e.g.

Wiens *et al.* 1993; Iidaka & Furukawa 1994). When phase transformation occurs in metastable mineral phases, it is not necessary to transform directly into a thermodynamically stable phase (or phase assemblage). Depending upon the P - T path, a metastable phase may transform to metastable phases (or phase assemblages) before transforming to the thermodynamically stable form. This phenomenon has recently been demonstrated in the postspinel transformation in forsterite (Mg_2SiO_4) by Kubo *et al.* (2000). Thus, there is no lack of possible metastable phase transformations to attribute to various earthquakes occurring between 70 and 670 km in subducted slabs.

The overlying slabs along the 650-km discontinuity were interpreted by Irifune & Ringwood (1987, 1993) as a piling up and buckling of the stable high-pressure products of the basaltic component of subducted oceanic lithosphere because these materials possess a density which is greater than that of the upper mantle and less than that of the lower mantle between the depths of 660–800 km. Moreover, these authors concluded that the buoyancy relationships would support the suggestion that the 650-km discontinuity provides a partial barrier to the entry of subducted slabs into the lower mantle. However, an unusual earthquake observed 200 km away from the inclined subducted slab under the Izu–Bonin Island region at a depth of 545 km was interpreted to occur in the bent slab lying horizontally on top of the 650-km discontinuity (Okino *et al.* 1989). This observation is consistent with an earthquake occurring at 25 km below the surface of the 80-km thick and bent slab. The interpretation of Okino *et al.* (1989) clearly implies that the horizontal part of the slab is identical to the inclined slab and is not the former upper basaltic part of the slab and that the earthquake is due to a phase transformation occurring in the metastable phases such as olivine. Many unusual deep earthquakes, which are several hundred kilometres away from the inclined subducted slab beneath the backarc of Tonga, were recently observed by Brudzinski & Chen (2000), who, however, reported that the seismogenic region is not associated with fast V_p .

In contradiction to the conclusion made by Irifune & Ringwood (1993) that the basaltic component of subducted slabs may not penetrate into the lower mantle, Kesson *et al.* (1994) proposed that this part of subducted slabs may enter into the lower mantle to explain the seismologically observed high velocities in the lower mantle.

The postulation of Kesson *et al.* (1994) was based on their study of phase transitions in basaltic glass at pressures between 0.45 and 1 Mb and their estimation of the density of the high-pressure products, which is marginally more dense (by 0.5 per cent) than the base of the lower mantle. Their estimation was based on a length extrapolation from estimated bulk moduli of these high-pressure products at the ambient condition to the P - T conditions at the base of the lower mantle. Regardless of the large uncertainties involved in these exercises, the arguments of both Irifune & Ringwood (1993) and Kesson *et al.* (1994) hinge solely on density contrast. However, the prior condition of a 'sinking' slab is not density. From earlier discussion that double seismic zones observed between 70–200 km and between 360–460 km were attributed to phase transformations in metastable mineral phases, it implies that the cold middle part of subducted slabs at depths between 400 and 500 km consists mostly of metastable olivine. The temperature difference between the coldest slab and the surrounding mantle at 600 km was estimated to be $\sim 400^\circ\text{C}$ by Ringwood (1991) and to be $\sim 300^\circ\text{C}$ by Ji & Zhao (1994). Thus, the temperature of the olivine at these depths cannot be 500°C colder than its surrounding mantle, which should be mainly either β - or γ -phase. The latter phases are some 8–10 per cent more dense than olivine. The 500°C temperature difference may only reduce the density contrast from 8–10 per cent to 7–9 per cent at the maximum. So, the existence of olivine in subducted slabs at depths below 400 km manifests that slabs do not 'sink' because of their great density and that slabs are most likely dragged into the mantle by mantle convection. In addition, many of the high-pressure phases considered by Irifune & Ringwood (1993) and Kesson *et al.* (1994) may not yield high velocities.

The role of hydrous phases in the subducted slabs was not considered to be relevant to the arguments of Irifune & Ringwood (1993) and Kesson *et al.* (1994). We have previously suggested that both hydroxyl-clinohumite and phase E are likely to be less compressible than forsterite, and that the hydrous β -phase is less compressible than β -phase. Thus, the lower density of these hydrous phases would guarantee them to have P -wave velocities higher than their corresponding anhydrous phases. Consequently, these hydrous phases (+ phase D, see below) may be responsible for the observed high velocities in horizontal slabs lying above the 650-km discontinuity. These hydrous phases are stable, but not necessary much colder and denser than their surrounding mantle.

At the moment, the only possible hydrous phase which is stable at the lower mantle conditions is phase D (Liu 1987; Frost & Fei 1998; Shieh *et al.* 1998). The ambient values of bulk sound velocity ($\Phi^{1/2}$) and density for the α -, β - and γ -phases of Mg_2SiO_4 can be derived from the data listed in Table 1 and are shown in Table 4. The same data for phase D, MgSiO_3 -perovskite and periclase are also listed in Table 4 for comparison. It can be seen that the density of phase D is comparable to that of the γ -phase, but its bulk sound velocity is nearly 5 per cent greater than that of the γ -phase. Thus, together with the hydrous β - and γ -phases, these hydrous phases may be responsible for the observed high velocities in slabs horizontally lying above the 650-km discontinuity as mentioned above. If the lower mantle is mainly composed of a mixture of MgSiO_3 -perovskite and periclase, the bulk sound velocity of phase D is comparable with that of the mixture, depending upon the ratio of MgSiO_3 -perovskite and periclase in the mixture. Thus, phase D might be responsible for the observed high velocities in the lower mantle in front of subducted slabs. The upper bound of the stability of phase D was studied by Shieh *et al.* (1998), who concluded that phase D should be stable up to about 1250 km at normal mantle P - T conditions. However, the stability boundary has a negative T - P

Table 4. Ambient bulk sound velocity ($\Phi_o^{1/2}$) and density (ρ_o) for most relevant anhydrous and hydrous mineral phases in the mantle.

Materials	$\Phi_o^{1/2}$ (km sec $^{-1}$)	ρ_o (g cm $^{-3}$)
Forsterite	6.34	3.21
β -phase	6.98	3.49
Hydrous β -phase	6.82	3.33
γ -phase	7.19	3.56
Hydrous γ -phase	6.68	3.47
MgSiO_3 -perovskite	7.74	4.10
Periclase	6.69	3.58
Phase D	7.56	3.50

$\Phi_o^{1/2} = (B_{S,o}/\rho_o)^{1/2}$; data of $B_{S,o}$ for forsterite, anhydrous and hydrous β - and γ -phases, see Table 1; for Mg -perovskite from Yeganeh-Haeri *et al.* (1989); for periclase from Jackson & Niesler (1982); for phase D from Frost & Fei (1998).

slope. So, if the temperature in front of the subducted slabs in the lower mantle is lower than its surrounding materials, the stability of phase D would extend to depths greater than 1250 km. Moreover, the stability of phase D determined by Shieh *et al.* (1998) is in a serpentine phase assemblage. So, the stability of phase D may extend to still greater depths in the true lower mantle phase assemblage.

Shieh *et al.* (1998) found that the phase assemblage containing phase D decomposes into the phase assemblage of MgSiO_3 -perovskite + periclase + ? with a negative dT/dP slope. The latter phase assemblage should be very close to those of the lower mantle itself. However, a boundary with a negative dT/dP slope is an endothermic reaction, so, the assemblage of MgSiO_3 -perovskite + periclase + ? may be colder than its surrounding lower mantle, which yields the observed high velocity and the assemblage may sink to the mantle-core boundary.

All the above suggestions, however, should be treated as very tentative. First, the bulk modulus of phase D reported by Frost & Fei (1998) is less reliable relative to those of other phases listed in Table 4. Second, the above suggestion was based on the values of bulk sound velocity calculated at ambient conditions. The use of the values of bulk sound velocity may not be a bad approach, because bulk sound velocity is normally proportional to P -wave velocity, which was the actual observed velocity in the seismological studies. However, the application of ambient data to the P - T conditions in the lower mantle is not typically appropriate. The exact situation must await future detailed studies of these materials at pressure and temperature conditions relevant to the deep mantle.

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